

✓ OPTIMAL RECOVERY OF NORMAL PARAFFINS FROM KEROSENES USING MOLECULAR SIEVE ADSORBENT

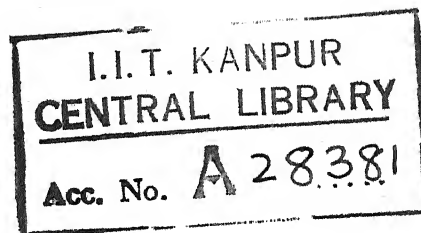
A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
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By
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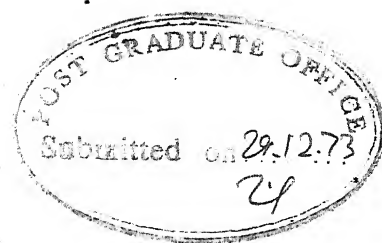
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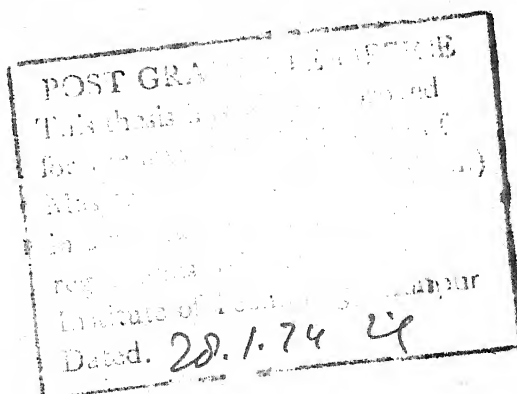


CERTIFICATE

It is certified that this work has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

An equipment for adsorptive separation of n-paraffins from kerosenes, capable of operation at high temperatures (400°C) and pressures (250 psig) was designed and fabricated. The objective was to seek optimum operating conditions for recovery of n-paraffins from Baroda straight run kerosene using LMS-5A. Pressure (range: 75-220 psig) and flow rate (range: 5-40 cc/min) turned out to be most effective parameters for the purpose of optimization. The optimum recovery of 4.10 cc/min. Kg of adsorbent was obtained at the optimum operating conditions of 195 psig (380°C) and 15 cc/min. Purity of recovered n-paraffins at these conditions was above 94% as measured by GLC and FIA methods. Smoke point of the effluent was monitored to make sure that it fulfils the requirement of marketable kerosene. Height of mass transfer zone and over-all mass transfer coefficient were calculated with the help of breakthrough curves and equilibrium loading on adsorbent by measuring the volume of n-paraffins. The experimental values of above three parameters came out to be 2.3 meter, 860 Kg/hr.cu.m. and 54 cc respectively.

Nitrogen, LPG and ammonia desorbing fluids were studied. out of the three desorbing fluids, ammonia was found the most efficient desorbent.

* * *

CHAPTER 1

INTRODUCTION

In the last decade, the use of normal paraffins in chemical industries has increased many fold. The manufacture of biodegradable detergents, requiring n-paraffins in the range of C_9-C_{17} , constitutes the most important use for these. The long chain alkanes are also converted to synthetic lubricants and fuel additives, plasticizers, industrial surfactants, floatation agents, solvents and raw material for protein synthesis by means of oxidation, halogenation, esterification, fermentation, etc. The demand for most of these products is steadily increasing at the rate of 15% per year in India. Large amounts of detergent alkylate and medicinal grade liquid paraffins are being imported in India every year.

All petroleum fractions contain varying amounts of several n-paraffins. The other constituents are olefins, branched chain paraffins, naphthenes and aromatics etc. The study of Chandra, et.al.⁽¹⁾ has shown that there is a wide variation in the occurrence of n-paraffins of the C_9 to C_{16} range in the straight run kerosenes of the various crudes. The content is of the range 20% by weight on kerosenes in imported crudes refined at coastal refineries, 33 to 40% in the different Gujrat crudes and of extremely low order of 2 to 8% in Nahorkatiya and Lakwa-Rudrasagar crudes of Assam region.

It should be possible to recover some or all of the n-paraffins from these fractions without entailing, serious deterioration in their quality. The recoverable amount of n-paraffins, which may be as high as 25,000 tons/year in 1972, may further grow to about half a million tons in 1980⁽²⁾. This will eliminate the import and will be a big boost to normal paraffin based industries. Since only Ankleshwar, Kalol and Navagam crude oils contain sizable amount of n-paraffins and have a larger margin for smoke point requirement (minimum requirement being of the order of 21 mm), they offer the greatest potential for the recovery of n-paraffins. The Ankleshwar kerosene (straight run) containing about 50% n-paraffins and with smoke point of 24 mm has been selected for the present study.

The overlapping of boiling points of n-paraffins with those of other hydrocarbons has rendered fractional distillation impractical method of separation. Urea Adduct method⁽³⁻⁵⁾ has been most extensively used in early days. The method is based on formation of an adduct between urea and n-paraffins and the separation of later from adducts is complicated. Furthermore, urea is not very selective and even some non-normal paraffins can participate in adduct formation. Another method of n-paraffin recovery involves use of selective adsorbents such as aluminosilicates (zeolites). These zeolites, may be minerals or may be synthesized have a regular crystalline form and are known commercially as microtaps or molecular sieves. Recently

ACC has started synthesizing molecular sieves in India at commercial scale.

The availability of n-paraffins in kerosenes and molecular sieves in India, suggests to develop a process for the optimum recovery. The design data necessary to develop a complete adsorption process have been discussed in detail in Appendix. The most important design data for the study are kinetic and equilibrium data. Many workers have reported these data for binary systems but multicomponent adsorption has not been investigated experimentally. Furthermore, the process conditions available in patents and literatures will not hold good for the Indian kerosene fractions. Based on these motivation, the present study has been undertaken to generate the kinetic and equilibrium data for adsorption process using fixed-bed of molecular sieves.

* * *

CHAPTER 2

BACKGROUND

The early investigators studied the naturally occurring zeolites - chabazite, heulandite and analcite. Of particular importance in the historical development of molecular sieves is the work of R.M. Barrer⁽⁶⁾ and his co-workers in Great Britain. As a direct result of these studies, investigators at Linde Company, Division of Union Carbide Corporation, became interested in the application of the natural zeolites to the gas-separation operations. By the early 1950's, the Linde team had synthesized some dozen crystalline zeolites. Some of these zeolites were analogous to the naturally occurring zeolites, but others were completely new compositions of matter. One of these had novel characteristics and was designated Type A. The Linde company is now in production and markets them under the trade name LMS (Linde Molecular Sieves) - Type 4A, 5A, 13X, Y and Z. Late in 1959 the Davison Chemical Division had synthesized them under the trademark "Microtraps".

The commercial zeolite (LMS-A) are alkali metal aluminosilicates with the composition $\text{Na}_{12} [12 \text{AlO}_2 \cdot 12 \text{SiO}_2] \text{NaAlO}_2 \cdot 29 \text{H}_2\text{O}$. One of the main features of the structure⁽⁷⁻⁹⁾ is its well defined main channels which run parallel to the cubic axes and have a minimum free diameter of 4.2\AA . The structure comprises 3 different types of cavities.

The largest cavity can hold a sphere with a diameter of 11.4\AA . These large cavities linked up by 8-membered rings form the unique main channels of the structure. The smaller isolated cavity is also roughly spherical in shape having an internal diameter of about 6.6\AA . The free diameter of these 6-membered rings is found to be 2.5\AA . The replacement of sodium ions with calcium ions enlarges the size of these windows, so straight chain hydrocarbons are readily adsorbed but branched chain hydrocarbons are excluded. Removal of crystal water leaves a stable crystalline solid containing mutually connected intracrystalline voids amounting to 45 volume percent of the zeolite. The Type-A zeolites have an internal surface area of 700-800 square meters per gram and an external area of 1-3 square meters per gram. The volume of the voids is 0.28 and 0.35 cubic centimeter per gram for Type A and X respectively.

These molecular sieves have all cavities and windows of uniform size. This uniformity of pore size enables it in sieving of molecules. The designation of Types 4A, 5A, X and Y characterizes the size of their cavities and windows. The mean cross-sectional diameter of n-paraffin molecules is 4.9\AA whereas iso-paraffins and cyclic molecules have minimum cross sectional diameter 5 to 6\AA . The naphthenes and aromatics have mean cross-sectional diameter greater than 6\AA . Thus under adsorptive conditions, if a mixture of hydrocarbons is passed through a bed of LMS-5A, the n-paraffins will be selectively adsorbed in the molecular sieves and the rest, which are larger

will not be adsorbed. The selective adsorption is reported⁽¹⁰⁾ to be based on four properties of the molecular sieves (MS).

- (1) M.S. adsorb small molecules but not large molecules and hence separation can be made on the basis of size.
- (2) M.S. have a high adsorption capacity even at low adsorbate concentration.
- (3) M.S. have a high affinity for unsaturated organic compounds.
- (4) M.S. have a high affinity for polar molecules.

Activation and Regeneration of Molecular Sieve:

The design and operation of the activation cycle has a direct influence on the adsorptive capacity or efficiency of the molecular sieve. Obviously, if activation is incomplete some material will be present in the bed at the start of the next adsorption cycle.⁽¹⁰⁾ Thus, the activation is a critical phase of IMS technology. There are three steps to the common activation cycle: heating, purging and cooling. For analytical purposes the sieve is activated at 500°C for 4 hours. Molecular sieves have also been improved by contacting with liquid water below 80°C for 4 hours followed by drying.⁽¹¹⁾ Another method used for activating the sieve is by heating it under vacuum. Ammonia has been recommended as the best desorbing agent.⁽¹²⁾ Because of its basicity, ammonia suppresses the catalytic activity of molecular sieves and thus lowers the rate at which adsorption capacity is lost due to hydrocarbon coking. The

carboneous deposits are removed by oxidation. Schumacher and York⁽¹³⁾ activated the molecular sieve column by passing hot nitrogen at 350°C for a total time of 2½ hours, at the rate of ~0.44 SCF per minute. The adsorbent was regenerated by passing hot air at 340°C for 24 hours.⁽¹⁴⁾ The adsorbent was regenerated in air at 360°C in a forced convection oven for 200 hours.⁽¹⁵⁾

This is the desorption step, where one process differs from other. Molex process⁽¹⁶⁾ uses low boiling hydrocarbons for desorption of n-paraffins. The Isosiv process⁽¹⁷⁾ of Linde Company operates on an isothermal pressure swing cycle. The adsorption is carried out in vapor phase and pressure swing cycle is used to desorb n-paraffins at reduced pressures.^(17,18) The British Petroleum Company process was developed for the extraction of n-paraffins from gas oil.⁽¹⁸⁾ The adsorption is carried out in vapor phase and desorption is done with n-pentane purge. The Texaco Selective Finishing Process is employed to upgrade the octane number of catalytic reformat, light or even heavy straight run naphtha.^(17,19,20,21) The parax process was developed by VEB Leuna works "Walter Ulbricht", East Germany for production of C₁₀ to C₁₈ n-paraffins from petroleum fractions in the range of 180° to 320°C in different stages.⁽¹⁾

* * *

CHAPTER 3

LITERATURE REVIEW AND ANALYSIS

Adsorption of n-Paraffins on Molecular Sieves:

Recent industrial advances in the fields of separation and purification of gases and liquids have placed molecular sieve adsorption processes among the major separation operations used in some process industries. For the proper design of packed adsorption columns knowledge of the breakthrough characteristics of column is required. The problem of predicting breakthrough curves from basic kinetic and equilibrium data has attracted much attention. The breakthrough curve may be calculated, for any system of known kinetics, from the solution of the differential rate equation subject to the boundary conditions. In practice the differential equations are generally complex and full solutions have been obtained only for the simpler cases. Such data as are available show many apparent anomalies and inconsistencies and there is even disagreement over fundamentals. Eberly⁽²²⁾ has observed a substantial difference between the rate of adsorption and desorption of n-pentane from 5A zeolite whereas other workers^(23,24) studying the similar systems have found the rate of adsorption and desorption to be the same.

The simple model isotherms (Langmuir, Volmer, B.E.T. etc.) are not in general applicable to zeolitic sorbents. The break-

through curves calculated from these mechanistic models did not compare well at high concentration even for pure gases.⁽²⁵⁻²⁷⁾ A new approach suggested by Ruthven⁽²⁸⁾ based on the principles of statistical thermodynamics was used to interpret the equilibrium data for the sorption of light paraffins in 4A and 5A zeolites.⁽²⁹⁾ Even this approach has been limited to the region of low sorbate concentrations. This simplified statistical thermodynamic model was extended to the sorption of binary mixtures.⁽³⁰⁾ The predicted equilibrium data for sorption of C_2H_6 -n C_4H_{10} mixture in 5A zeolite compared well with limited experimental equilibrium data. The range of experimental equilibrium data for mixtures is limited and to provide a good test of the theory, further data are required over a wider range of sorbate concentrations and hydrocarbon mixtures. The theory, either for sorbates of equal molecular volume or when sorbate concentration is less than about 1 molecule per cavity, reduces to the ideal solution model of Myers and Prausnitz.⁽³¹⁾ The model provides a simple method of predicting multicomponent sorption equilibria from Henry constants for the pure components.

Recently Garg and Ruthven^(32, 24) have provided the asymptotic solutions and predicted the breakthrough curves for molecular sieve adsorption column. For column saturation, the limiting breakthrough curve is of the 'constant pattern' type. For the two cases of micropore and macropore diffusion control the forms of the constant pattern curves are calculated

from the solutions of the appropriate diffusion equations subject to the simplified boundary conditions appropriate for a long column. The theory needs experimental breakthrough curves for mixtures for verification. The experimental data of multicomponent mixture are limited and could not be verified for these systems.

Mass Transfer Zone (MTZ) Model:

Perhaps the simplest approach to correlating fixed-bed adsorption performance and the most useful for design purposes is the mass transfer zone model. This model proposed by Michaels⁽³³⁾ makes no assumption regarding the controlling adsorption rate mechanism. The model is based on the existence of an exchange zone of constant length across which the fluid concentration changes from $0.05 C_0$ to $0.95 C_0$. This zone is established at the top of the column and is assumed to move down the column with a constant velocity.

The working equation for the model is

$$H_z = \frac{H_T(\theta_E - \theta_B)}{F(\theta_E - \theta_B) + \theta_B} \quad (1)$$

The fraction of the mass transfer zone free of adsorbate, F , is obtained from a graphical integration utilizing the breakthrough curve. Equation (1) is then used to calculate H_z from the experimentally determined breakthrough, and exhaustion times. Gehrhardt and Kyle(1967)⁽¹⁴⁾ studied experimentally

the drying of benzyl alcohol by fixed beds of 5A molecular Sieves. Breakthrough curves were obtained for various bed heights, feed rates and feed concentrations. The results were well correlated in terms of the mass transfer zone model and H_z was found to be independent of bed height. The variation of H_z with feed rate was linear and H_z increases with increasing feed concentration. These findings are also in agreement with the observations of Nutter and Burnet⁽³⁴⁾ for the drying of air. Treybal⁽³⁵⁾ has extended the MTZ approach to the calculation of breakthrough curves. He assumed the mass transfer based on the fluid-film driving force and MTZ independent of concentration. The B.T.C. produced by this method was poor in agreement. When Treybal's derivation is altered by an expression based on a solid phase driving force, the breakthrough curve obtained was in better agreement with the experimentally obtained curve.

Schumacher and York⁽¹³⁾ determined the values of height of adsorption zone and over-all mass-transfer coefficient from experimentally measured breakthrough curves for the separation of n-Hexane from cyclohexane, benzene and 2,2, 4-trimethylpentane taking binary system at a time. The adsorption was carried out in liquid phase with limited study for vapor phase using LMS-5A. The effect of flow rate, adsorbent particle size, temperature, feed concentration and solvent system on the height of mass transfer zone and overall mass-transfer coefficient is reported.

For vapor-phase adsorption, the zone height was proportional to about 0.64 power of velocity for all solvent systems. His results agree fairly well with those of Kehat and Rosenkranz⁽³⁶⁾ whose zone heights for the vapor-phase adsorption of n-hexane from benzene by Type 5A molecular sieves were proportional to about the 0.57 power of velocity. The zone height, for the liquid phase adsorption, was unchanged/slightly decreased by doubling the feed temperature from 80° to 160°F. The overall mass transfer coefficients for vapor phase adsorption, increases with superficial velocity. They are less than those predicted by theory and also show a greater than expected velocity dependence. He compared the theoretical values calculated under the assumption of bulk diffusion in the pores. If Knudsen diffusion is assumed to control the mass transfer rate in the pellet, the value of $K_y a$ would be approximately halved.

Kehat and Rosenkranz⁽³⁶⁾ have done similar study of MTZ and overall mass transfer coefficient ($K_y a$) for n-hexane in benzene using 5A molecular sieves. The study was with respect to temperatures of 150° to 250°C, pressures of 40 to 150 psig., and Reynolds numbers of 2.2 to 47. The height of MTZ increased with increased Reynolds number and decreased with increased pressure. The effect of temperature on the height of MTZ was not significant. The adsorptive capacity of molecular sieve 5A decreased with increased temperature and Reynolds number,

while increase in pressure increased the adsorptive capacity. The increased values of overall mass transfer coefficients with increased temperature and pressure were in conformity with the expected behavior, but the decreased values of $K_y a$ with increased Reynolds number was unusual. The same type of study with the same system was carried by Schumacher and York, where these effects were found to be of a reverse nature. The effect was attributed to the requirement of orientation of the adsorbed molecules at the surface openings of the molecular sieves.

Overall mass transfer coefficients, calculated by the method of Hougen and Marshall⁽³⁷⁾ were obtained by Kehat and Rosenkranz. Totally different mass transfer coefficients, using the mass transfer zone equation of Michaels were obtained by Schumacher and York.

Recovery of n-Paraffins:

Adsorption of the n-paraffins on the M.S. normally occurs rapidly. Desorption on the other hand is relatively slow.⁽³⁶⁾ The rate at which n-paraffins can be desorbed from the sieve, and, thus the length of the desorption step is usually the limiting factor which sets the required cycle time for the process. Generally, it is desirable to use as short a cycle as possible in order to maximize the n-paraffin production rate for a given amount of molecular sieve. Short cycles can not be used without relatively rapid n-paraffin desorption rates.

Very little has been published about the desorption part of the cycle. Nelson and Walker⁽³⁸⁾ studied the desorption of propane from molecular sieve - 5A. Peterson and Redlich⁽³⁹⁾ made a very thorough study of desorption of n-paraffins at very low pressures from a bed of about 1 gm of molecular sieve - 5A and presented an empirical correlation for the rates of desorption.

The desorption is done either by raising the temperature of the bed or by some means reducing the equilibrium pressure of the adsorbate on the molecular sieve bed. Reduction in partial pressure is done by purging with some other gas like nitrogen or low boiling n-paraffins. At elevated temperature, if a polar gas (like ammonia and carbondioxide) is passed, the desorption time taken will be the least of all.⁽⁴⁰⁾ There are several basic adsorption process cycles which involve adsorption and desorption. These can be classified as thermal swing, pressure swing, purge gas stripping, displacement and a combination cycle.^(10,41) The thermal swing cycle is suitable for low boiling fractions because high boiling fractions of n-paraffins may undergo cracking.⁽⁴⁰⁾ Pressure swing cycle and purging are suitable for low boiling n-paraffins.⁽⁴⁰⁾ In displacement desorption an adsorbable material, which is more strongly adsorbed than the material being desorbed, is used. Higher molecular weight n-paraffins can be used to desorb less strongly adsorbed lower molecular weight n-paraffins. But the efficiency of the adsorption bed is lowered in subsequent adsorption step.

Displacement desorption using low boiling n-paraffins technique involves two primary driving forces. Firstly it acts as a purging medium and secondly at a later stage of desorption step, its high concentration in bulk phase causes displacement of adsorbed n-paraffins.

Asher, et.al.⁽¹²⁾ described a novel adsorption process, the Ensorb Process, developed by ESSO Research and Engineering CO. for the recovery of high purity n-paraffins using ammonia as a desorbing agent. Paraffins upto C_{33} have been recovered by this process in pilot plant equipment. The process is operated at constant temperature (260-370°C) and constant pressure (15-50 psia). Adsorption takes place in vapor phase. It does not require any special step to recover adsorbed ammonia. Kehat and Heineman⁽⁴²⁾ have carried out the study of desorption times of linear hydrocarbons C_6 to C_{10} . The desorption was carried out under vacuum of 2 to 5 mm of Hg from a large bed of molecular sieve - 5A. The times required for 50%, 95% and complete recovery of n-paraffins were 20 seconds, 5 minutes and 20 minutes respectively.

Analysis

Molecular sieve adsorption has been effectively combined with gas chromatography for determining the distribution of n-paraffins in petroleum fractions. The subtractive GLC methods involve duplicate chromatograms of the oils with and without a precolumn of 5A type sieve.⁽⁴³⁾ Comparison of the chromato-

grams reveals the contribution of n-paraffins to the overall spectrum. The columns used were 26% silicone grease E301 on 30-60 mesh 'Sil-O-cel' furnace brick and 1.6% squalane on 30-60 mesh molecular sieve 5A.

Subtraction and re-elution GLC methods involve chromatography of an oil while removing the n-paraffins in a M.S. pre-column and subsequent elution of the sieve bed at elevated temperature to obtain chromatogram of the n-paraffin.^(44,45,46) Boxter and Keen⁽⁴⁴⁾ have compared the performance of columns, household detergent containing about 17% of an alkyl aryl sulfonate and Apizon-L grease for various n-paraffins. Sodhi and Chandra⁽⁴⁷⁾ have carried out the complete analysis of kerosene fraction from various sources. Total n-paraffins and the carbon number distribution of the n-paraffins separated by MS, 5A was determined by GLC analysis.

* * *

CHAPTER 4

ADSORBER DESIGN THEORY

The operation of a fixed-bed adsorber can perhaps be best understood by considering a binary fluid in which one component (C_0) is strongly adsorbed. This binary mixture is then passed continuously through the adsorbent bed. The concentration profile, along the length of adsorber and in the effluent as adsorption occurs, can best be illustrated by considering Fig. A-2²

At point 1, the adsorbent adsorbs the solute very rapidly and very efficiently and the concentration of solute in the effluent is negligible. The distribution of the solute in the bed is shown in Fig. A-2. The uppermost layer is completely saturated and the bulk of the adsorption takes place in a very narrow band of the adsorbent. The concentration changes very rapidly in this narrow band known as the adsorption zone. As flow and adsorption continues, the adsorption zone moves down the column as shown at point 2.

At point 3, the adsorption zone has just reached the bottom of the column, the solute concentration now arises rapidly and for the first time is considerable. This is known as the "break point". As the flow continues the adsorption zone completely leaves the adsorbent bed, and the solute concentration in the effluents rapidly approaches the initial concentration. This is shown by point 4. The curve from point 3 to 4 is termed

"the breakthrough curve". If the flow continues, the bed is no longer effective and equilibrium has been reached between the adsorbate and adsorbent.

The shape and time of appearance of the breakthrough curve influence the method of operating the fixed bed adsorber. In general, the curves are S-shaped but can be steep or relatively flat and in some cases distorted. An infinitely rapid adsorption would give a vertical line at the breakthrough point. The actual rate and the mechanism of the adsorption process, concentration of the adsorbate, the nature of the equilibrium fluid velocity and condition of the adsorbate are important factors that contribute to the shape of the adsorption curve.

The specification (diameter and height) of a fixed-bed adsorber depend upon the desired amount and extent of separation. Detailed design requires the prediction of either the complete breakthrough curve or the height of the adsorption zone, and also the bed capacity within the zone. The design method followed in this work is the mass transfer zone approach suggested by Michaels.⁽³³⁾ The adsorption zone is defined herein as that portion of the bed over which the fluid phase concentration changes from 0 to 100% of the feed concentration. This approach is based on the important assumption that the height and velocity of the adsorption zone remain constant as the zone moves through the bed. Glueckauf and Coates⁽⁴⁹⁾ point out that in actual practice, zones (obtained with n-hexane on molecular sieves

type 5A) are of nearly constant height.

The height of the MTZ (Mass Transfer Zone) can be calculated from experimental breakthrough curve by two independent equations. The first is based on constant width, constant velocity MTZ, and a zone formation time which is assumed proportional to the fractional saturation of the adsorbent within the zone at the breakthrough point.

The zone height, H_z , is expressed as

$$H_z = H_T \frac{(\theta_E - \theta_B)}{(\theta_E - \theta_B)F + \theta_B} \quad (2) \quad (1)$$

where H_T is the total bed height, θ_E is exhaust point, θ_B is breakthrough point and F is the fractional ability of the adsorbent within the adsorption zone to adsorb additional solute.

The second equation for determining the zone height is based on a solute material balance within the adsorption zone.

$$H_z = \frac{Q_a}{A \rho_s X_s F} \quad (3) \quad (2)$$

where Q_a is the quantity of n-paraffins adsorbed between the breakthrough and exhaustion points, A is the cross sectional area of the column, ρ_s is the bulk density of solute free LMS 5A and X_s is the equilibrium loading of n-paraffins. Agreement between equations (1) and (2) will confirm the validity of the assumptions inherent in equation (1).

The height of MTZ can also be derived from the expression for the rate of mass transfer in the adsorption zone.

$$H_z = \frac{G_s}{K_{ya}} \int_{y_b}^{y_e} \frac{dy}{y-y^*} = \frac{G_s N_t}{K_{ya}} \quad (4)$$

where G_s is the superficial mass flow rate of solvent, K_{ya} is the overall mass transfer coefficient, N_t is the overall number of transfer units, y is the solvent concentrations of the fluid stream at any point in the adsorption zone. y^* is solvent concentration in equilibrium with the adsorbent. y_b is solvent concentration at the breakthrough point and y_e is solvent concentration at the exhaustion point. Equation (3) is based on the assumption that K_{ya} is constant throughout the adsorption zone. N_t was calculated assuming irreversible adsorption as indicated by Barry and Roberts'. By this assumption, y^* in equation 3 is zero, and the value of N_t between the limits of 0.05 and 0.95 is 2.94 for all experimental runs. The overall resistance to mass transfer in molecular sieves can be envisioned to be composed of at least three individual resistances to diffusion. (1) external film resistance, (2) intercrystalline diffusion resistance and (3) intracrystalline diffusion resistance.

Scope of Present Study:

The present study was undertaken to generate equilibrium and kinetic data required for process of recovery of n-paraffins from straight run kerosene using fixed-bed adsorption column.

These data then can be used to test the validity of theoretical prediction of these data for mixtures. The various design considerations have been discussed in Appendix. Out of them only pressure drop, equilibrium and kinetic studies were carried out for the optimum recovery. Analysing the past work carried out for the separation of n-paraffins from benzene, naphthanes and olefins using LMS 5A, the most important parameters affecting the optimum recovery seem to be temperature, pressure and flow rates. In the vapor phase adsorption, temperature has got insignificant effect on optimum recovery. The liquid phase study has already been done by Mahto⁽²⁾ et.al using Assam Refinery kerosene. Thus only two parameters, pressure and flow rate, have been selected for detailed investigation.

To achieve the above objective efficiently, experiments were carried out according to a modified two level factorial design. After the first cycle of experimentation was over, EVOP method was applied to search the useful direction of experimentations. Once the optimum conditions were obtained, height of mass transfer zone, overall mass transfer coefficient and bed capacity were calculated.

A limited study was also carried out to study the effect of different desorbing fluids (nitrogen, liquified petroleum gas (Indane) and ammonia) on the rate of recovery of normal paraffins.

* * *

CHAPTER 5

EXPERIMENTAL INVESTIGATION

A. Experimental Apparatus:

A schematic diagram of the experimental apparatus used is shown in Fig. 1.

Adsorption Column:

It consisted of a copper pipe 82 cm long, 4.45 cm. O.D. and 3.7 cm I.D. fitted with caps on both ends. Stainless steel tubing 15 cm long and 1.27 cm. O.D. (0.84 cm. I.D.) were attached to these caps. To make the dismantling convenient (without disturbing the rest of apparatus) both top and bottom connections were made through union joints. Tee joints were connected to both ends of column, one connection of each going through the vaporizer and the other to the condensers. One 1/4" stainless steel needle valve was placed on each line immediately after tee joint. A Bourden tube pressure gauge (0-300 psi) and a thermocouple were placed just after the needle valve on the tubing going to the vaporizer. The column was packed with 630 gms of LMS-5A in the form of 1/16" pellets. In order to prevent the choking of flow line in the bottom adsorber, a wire gauge was placed between the cap and the adsorber. Two thermocouples (chromel-Alumel, inserted with asbestos tube) were inserted horizontally through the furnace at one-third distance from each end of the column. The thermocouples were touching the outer

surface of copper pipe. The column was inserted into a tubular furnace, which was 2.25" I.D. and 32" long and was held in vertical position.

Feed Tank:

The feed tank was made out of a stainless steel pipe, 12" long and 4 $\frac{1}{4}$ " O.D. (4" I.D.) fitted with a Bourden pressure gauge (0-40 atm). One stainless steel tubing 15 cm long and 1.27 cm O.D. (0.8 cm. I.D.) with a device for charging liquid kerosene was attached to the pipe for introducing nitrogen gas. Another stainless steel tube 45 cm long and 1.27 cm O.D. (0.8 cm I.D.) was fitted (with a clearance of 3 cm from bottom) to the top of the pipe for pumping the liquid kerosene at high pressure.

Furnace/Heater:

The furnace or the heater used to raise the temperature of the adsorption column was made from a silliminite tube of 2 $\frac{1}{4}$ " I.D. and 32" long. Since it was difficult to maintain a uniform temperature distribution over the entire length, it was decided to divide the furnace into two sections; each section provided with its own temperature controller. Both top and bottom sections were wound with 16 gauge nichrome wire (resistances 5 ohms and 9 ohms respectively). The thermocouples for both the controllers were inserted into the furnace at 11" and 24" from the top. The temperature was controlled within $\pm 5^{\circ}\text{C}$ in both these sections. The measured variation

in temperature along the length of the furnace was not more than 10°C.

Preheater and Vaporizer:

The evaporator consisted of a coil of 1/4" copper tubing which was 1.8 meters long. A thermocouple (chromel-Alumel) was soldered at the end of the vaporizer column and was connected to a pyrometer. The column was kept inside the Lindeburg furnace (type-54241), supplied with a precise automatic controller.

Condensers:

The denormalized kerosene vapor was condensed in a coil of 1/4" copper tubing, 20 feet long, encased in a M.S. shell. Normal Normal paraffins were condensed in a shell and tube condenser. The tube for paraffin condenser was made of copper (1" O.D., 3/4" I.D. and 30" long) encased in a brass shell.

Flowmeter:

To measure the flow rate of the feed to the adsorption column, a precision rotameter made by F.W. Dwyer Manufacturing Co., having a measuring range of 10 to 50 cc of water per minute, was used. Appropriate calibration was done for kerosene feed.

Sampling and Collection:

The condensed denormalized kerosene coming out from the bottom condenser was collected at the interval of 1 minute in test tubes. Normal paraffins coming out the top condenser

along with the desorbent were collected in a conical flask fitted with two outlet glass tubes. The desorbent (ammonia) was taken out from the top outlet and was dissolved in a water tank and liquid n-paraffins were taken out from the bottom outlet of the conical flask.

B. Experimental Procedure:

The liquid kerosene was charged into the feed tank and was pressurized with nitrogen gas upto the pressure selected for the run. The pressure was controlled with the help of two needle valves No. 1 and No.2 (as numbered in Fig. 1). The flow rate was controlled through a needle valve (No.4) and measured with a rotameter placed in the line. The feed was allowed to pass through the vaporizer column and the adsorption column maintained at the same temperature as vaporizer. The effluent stream was cooled to condense all paraffins and was collected. After the adsorption was complete the feed was stopped. The adsorbed n-paraffins were subsequently desorbed.

Calibration of Rotameter:

The particular rotameter used was calibrated for flow of water. As kerosene has got different viscosity than water, it had to be calibrated for kerosene. The valves No. 4 and No.7 were closed and valve No.6 was opened. Flow calibration was made with kerosene pressurized to some moderate pressure. The liquid coming out of the union joint just before the entrance to the

adsorption column, was collected in a measuring cylinder for a known interval of time (recorded by a stop watch). An average of three readings was taken for each flow rate.

Activation of the Molecular Sieves:

The furnace temperature was raised to about 500°C which in turn raised the temperature of the sieve column to about 500°C. After about one hour, nitrogen gas at 5 psig (preheated to about 500°C in the preheater) was allowed to pass through the column. This purged the column of ammonia adsorbed on the molecular sieves during the desorption cycle. After half an hour the nitrogen supply was cut off and the column was allowed to cool. It was then ready for reuse.

Adsorption:

The sieve column was activated as described above. Its temperature was raised to a level at which adsorption was to be carried. The temperature of the preheater was also raised to the same level. Kerosene was taken in the feed tank and was pressurized with nitrogen gas upto the pressure selected for the run. Valve No.6 was closed and valve No.4 was operated. After a few seconds the Bourden gauge No.11 was showing the same pressure as the Bourden gauge No.10. At this condition valve No. 6 was operated to give the desired flow rate and pressure in the column. During adsorption, valves No.7 and No.8 were kept closed. The effluent from the bottom (after adsorption) was allowed to pass through

condenser No.19. Ice cold water was circulated in the shell side of this condenser with a Tullu pump. During adsorption the pressure and flow rate were controlled manually. After the equilibrium was reached, the adsorption process was stopped by closing feed valve No.4. In the beginning portion of the adsorption cycle small samples of the effluent were collected in test tubes after every one minute.

During later portion of the adsorption cycle, samples were collected after every two minute. It was planned to ascertain the break point more precisely. Refractive index was monitored for these samples on an Abbe Refractometer. S-shaped refractive index versus time curve was obtained; levelling off of the curve marked the saturation of the column. Before the desorption process was started (to activate the molecular sieve), nitrogen gas at 5 psig was blown through the column to remove any traces of feed present in the flow lines.

Desorption:

The n-paraffins adsorbed on the molecular sieves were desorbed by sweeping the column with ammonia gas at 5 psig. Two desorption cycles were carried out one with nitrogen and the other one with LPG. In the case when ammonia was used as a desorbing agent, the column temperature was maintained at adsorption temperature level. When nitrogen and LPG were used for desorption, the temperature of the column was raised by about

100°C. The desorbants were preheated and passed through the bottom of the adsorption column. Valves No.7 and 8 were kept open and valves No.6 and 9 were kept closed. Desorbed n-paraffins along with the desorbant (ammonia) were collected in the special conical flask described earlier. Ammonia was allowed to pass through the top outlet and was dissolved in the water tank, while the n-paraffins were taken out from bottom of the flask, which was fitted with a stop-cock. Desorption process was continued until all the adsorbed n-paraffins were recovered.

Analysis:

Small samples about 1 cc of the effluent from condenser No.19 were collected in test tubes for each run at regular intervals of time. The denormalized kerosene, coming out of the condenser No.19, was collected and its volume recorded with the help of graduated cylinder. Volume of samples was also added to the volume of denormalized kerosene. Smoke point was monitored for this denormalized stock on a smoke point lamp. The apparatus and procedure used for this analysis were the same as that given in ASTM (Designation: D1322-59T).

The n-paraffins were analysed for the content of the saturates, the non-aromatic olefins, and the aromatics using an FIA method. The apparatus and procedure followed in this analysis were according to ASTM (Designation: D1319-61T). Further, the purity of n-paraffins recovered was checked using the GLC analysis.

C. Materials Used:

The following materials were used in the present investigation:

(1) Straight run kerosene (140°-300°C) was obtained from Gujrat Refinery which processes Ankleshwar crude. The volume percentage of n-paraffins was 50 (from personal communication to Gujarat Refinery). The smoke point and density were 24 mm and 0.7970 gm/cc respectively.

| (2) | <u>Name of Material</u> | <u>Purity</u> | <u>Supplier</u> |
|-----|-------------------------------|------------------|---|
| 1. | Nitrogen Gas | 99.5 mole% | Industrial Gases Ltd., Kanpur |
| 2. | Commercial Ammonia | - | Kanpur |
| 3. | LPG (Indane) | - | Kanpur |
| 4. | n-Nonane | 98.5% | BDH Chem. Ltd., Poole England |
| 5. | n-Decane | 95% | -do- |
| 6. | n-Cetane | 95% | -do- |
| 7. | n-Heptadecane (L.R.) | Pure | Koch-Light Laboratories Ltd., England |
| 8. | n-Tridecane | 95% | Fluka AG, Switzerland |
| 9. | Silica Gel (100-200 mesh) | Lab. Chem. | Sarabhai M. Chemical Ltd. Bombay |
| 10. | Iso-Proylalcohol | L.R. | HPC, Bombay |
| 11. | Sudan III (Dyes) | IP156/58T | L. Light & Co. Ltd., Colnbrook, England |
| 12. | Linde Molecular Sieves -5A | 1/16" Pellets | Linde Company, Division of Union Carbide Corporation, U.S.A. |

CHAPTER 6

RESULTS AND DISCUSSION

A. Experimental Results

The straight run kerosene (boiling range: 140° to 300°C) obtained from Gujrat Refinery was used in the present study. The breakthrough curves were plotted for various flow rates and pressures. The optimum adsorptive conditions were investigated using the objective function:

$$S = \frac{\text{Volume of n-paraffins recovered}}{\text{Total time for recovery} \times \text{weight of molecular sieves in the bed.}}$$

Volume of n-paraffins, total time and weight of IMS-5A were measured in cubic centimeter, minute and kilogram respectively. Time measurement was started when the first drop appeared out of the condenser No.19. All the runs were taken in duplicate with the same adsorbent bed. Even after 8-10 cycles of operation, the bed was capable of repeating its performance within 5% reproducible results. For obtaining breakthrough curves, averaged (smoothed) data were plotted.

Runs were made at various operating conditions in the range of 5 cc to 40 cc per minute flow rate and 75 to 245 psig pressure. The temperature of feed was adjusted such that it was slightly higher than the boiling point of kerosene corresponding to the selected pressure. Thus the independent parameters to be optimized were pressures and flow rates only. Then the height

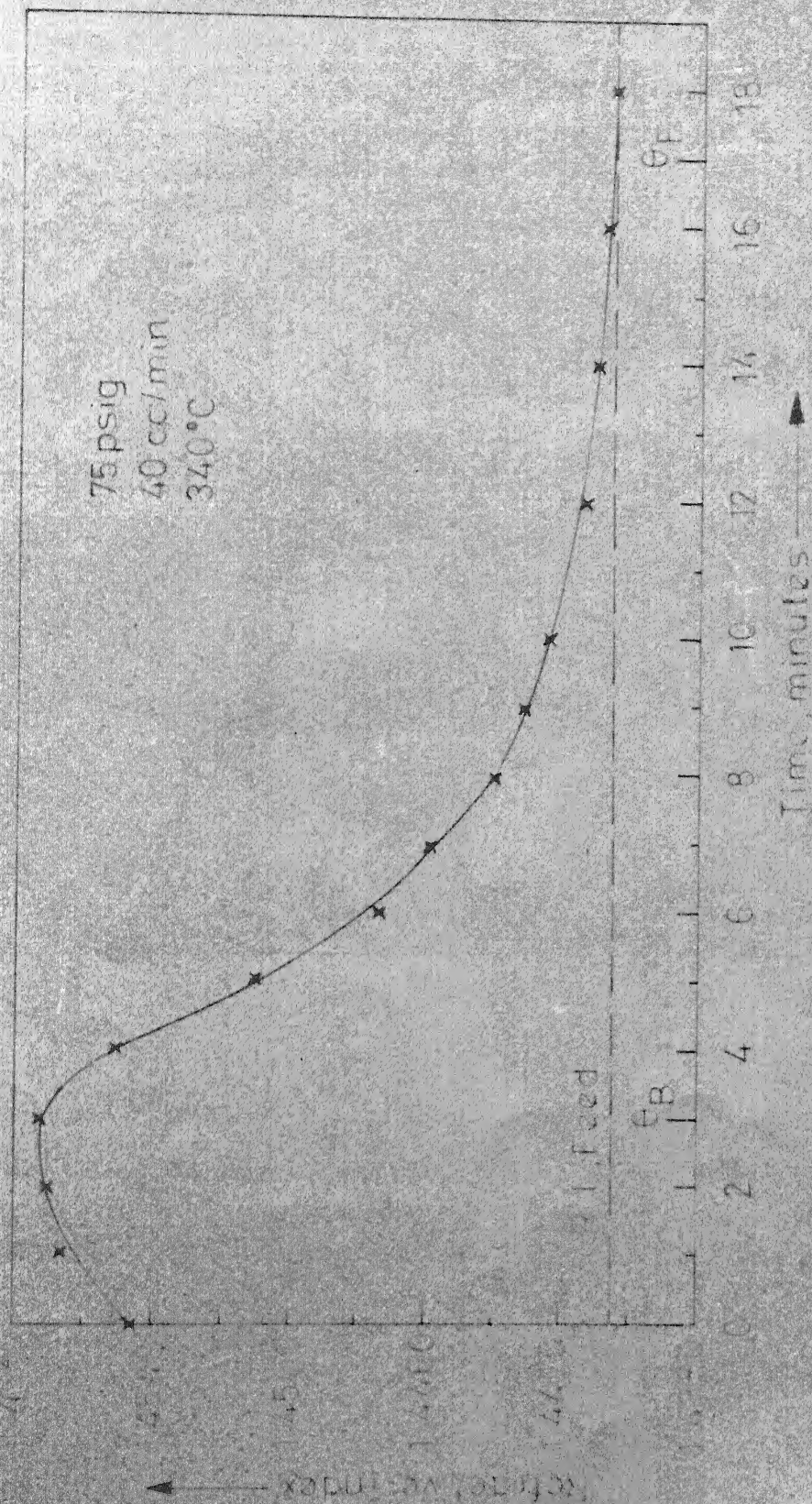


Fig. 2 - Breakthrough curve for Kerosene.

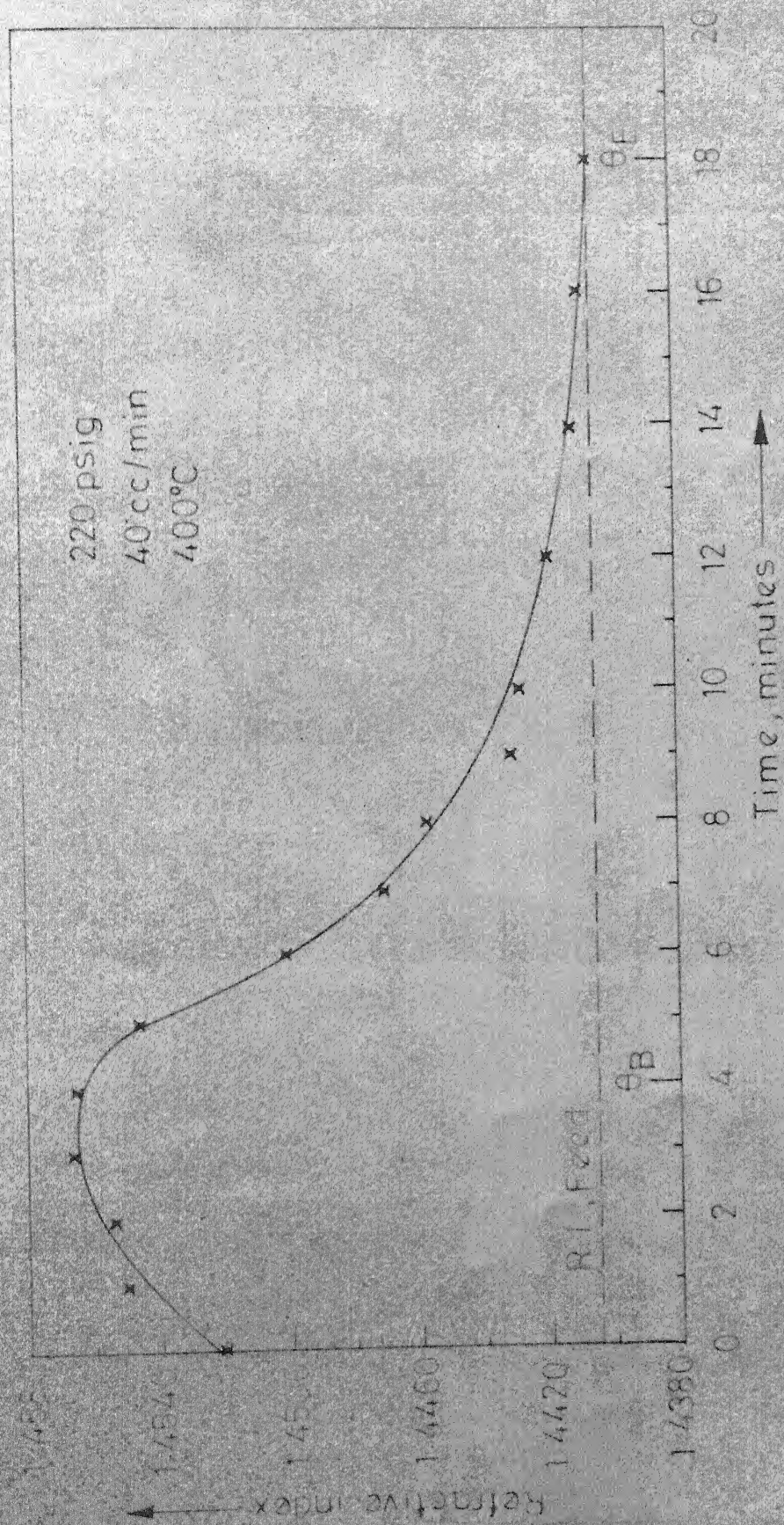


Fig 3 - Breakthrough curve for Kerosene

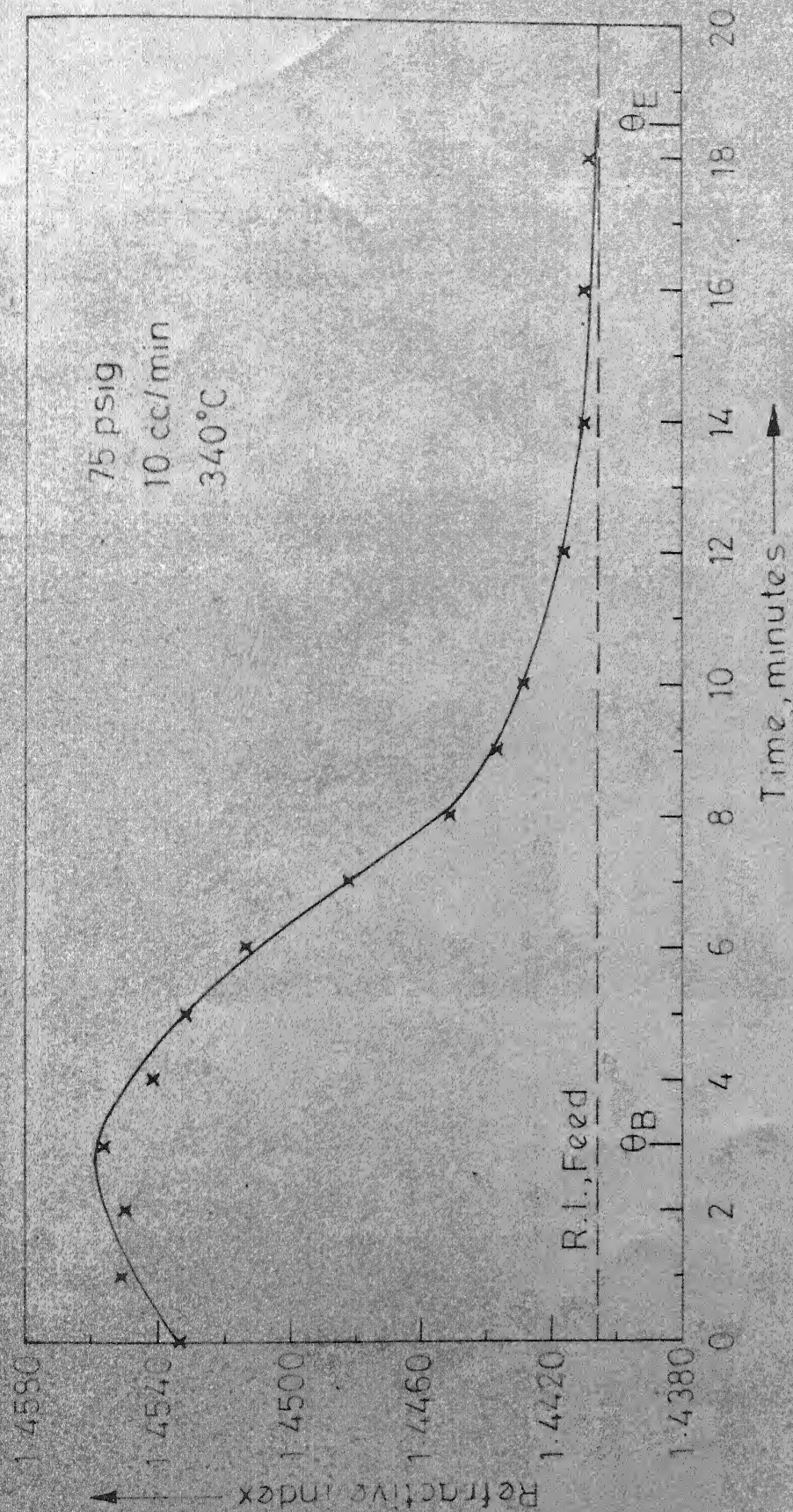


Fig 4 - Breakthrough curve for Kerosene

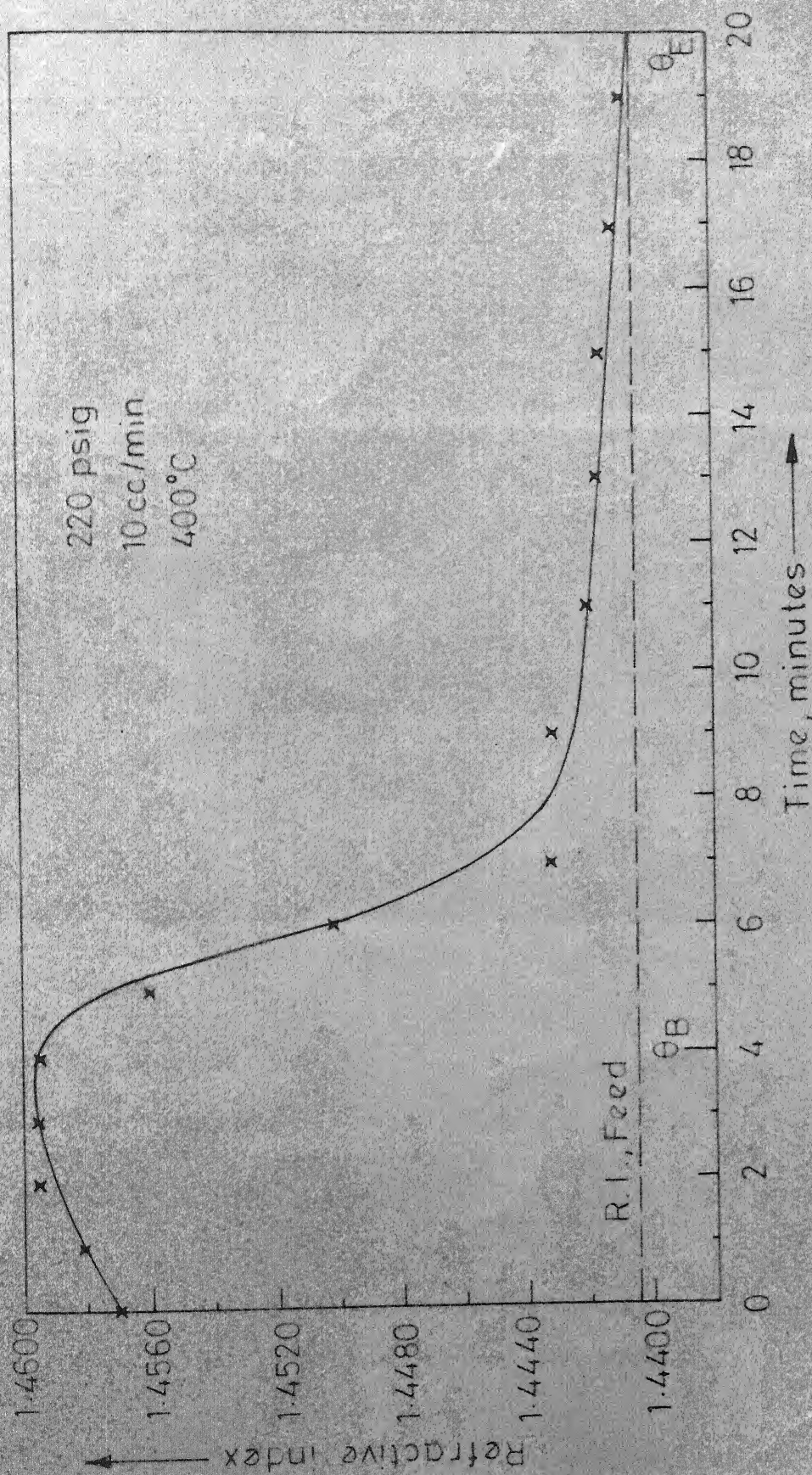


Fig 5 - Breakthrough curve for Kerosene.

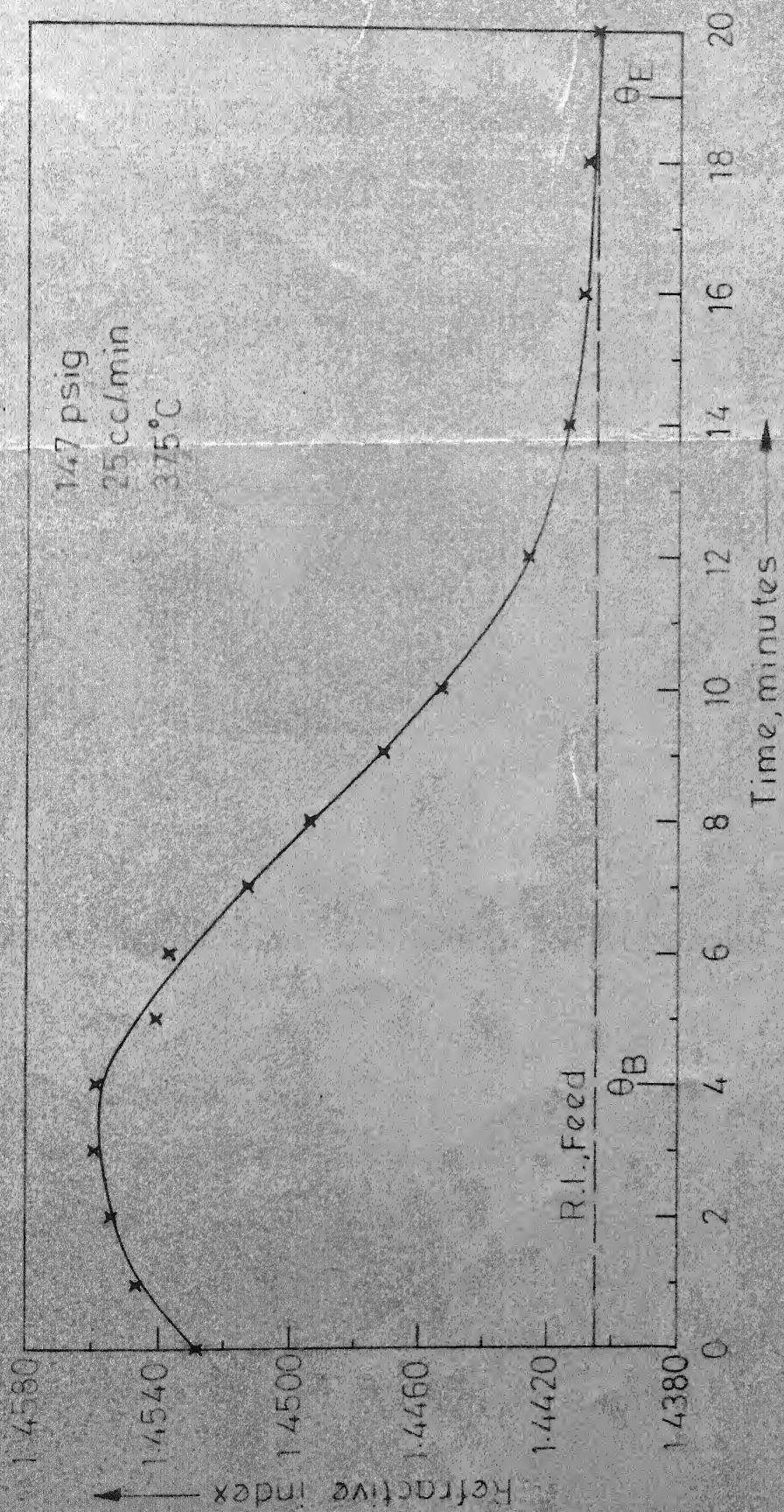


Fig. 6 - Breakthrough curve for Kerosene.

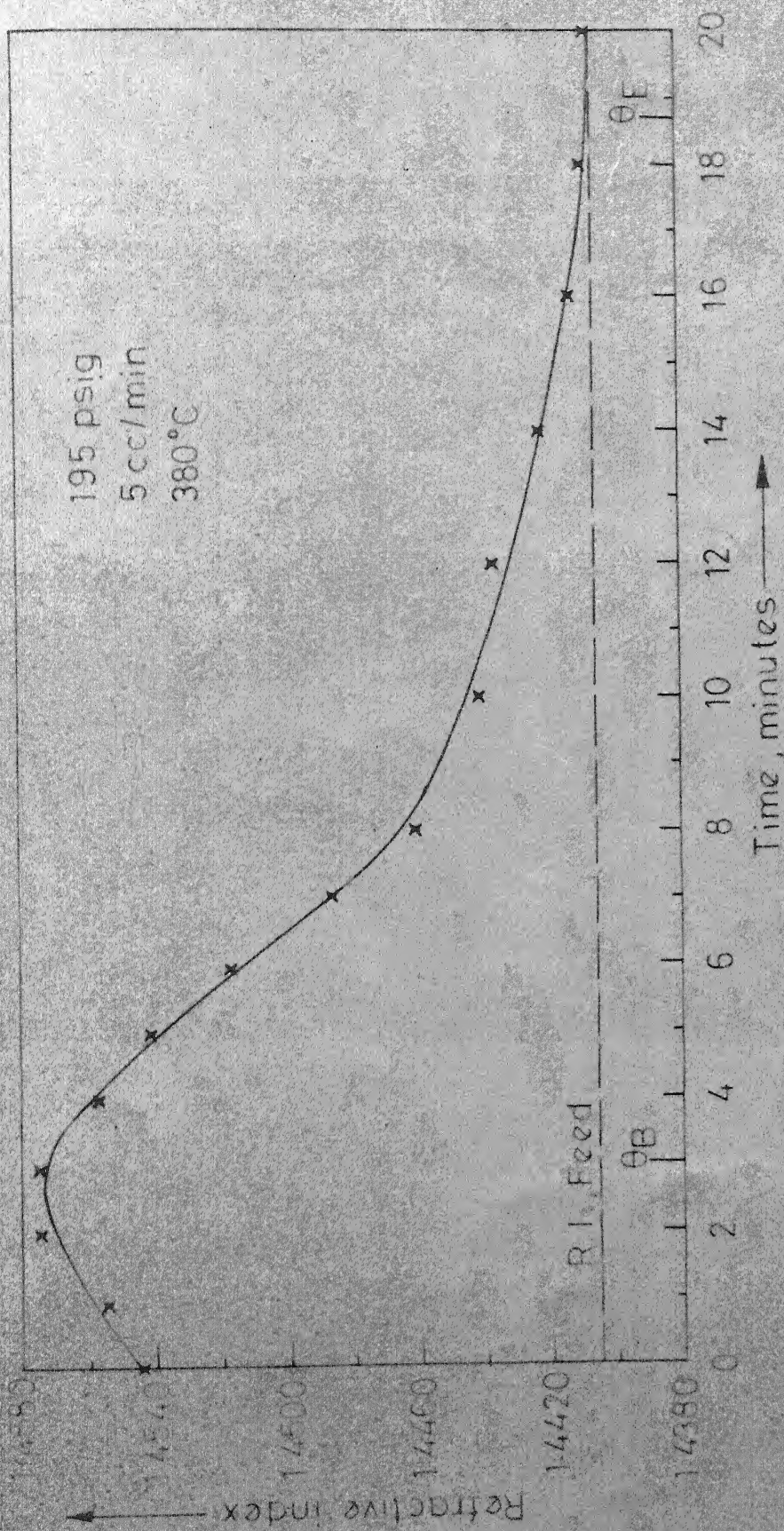


Fig 7 - Breakthrough curve for Kerosene.

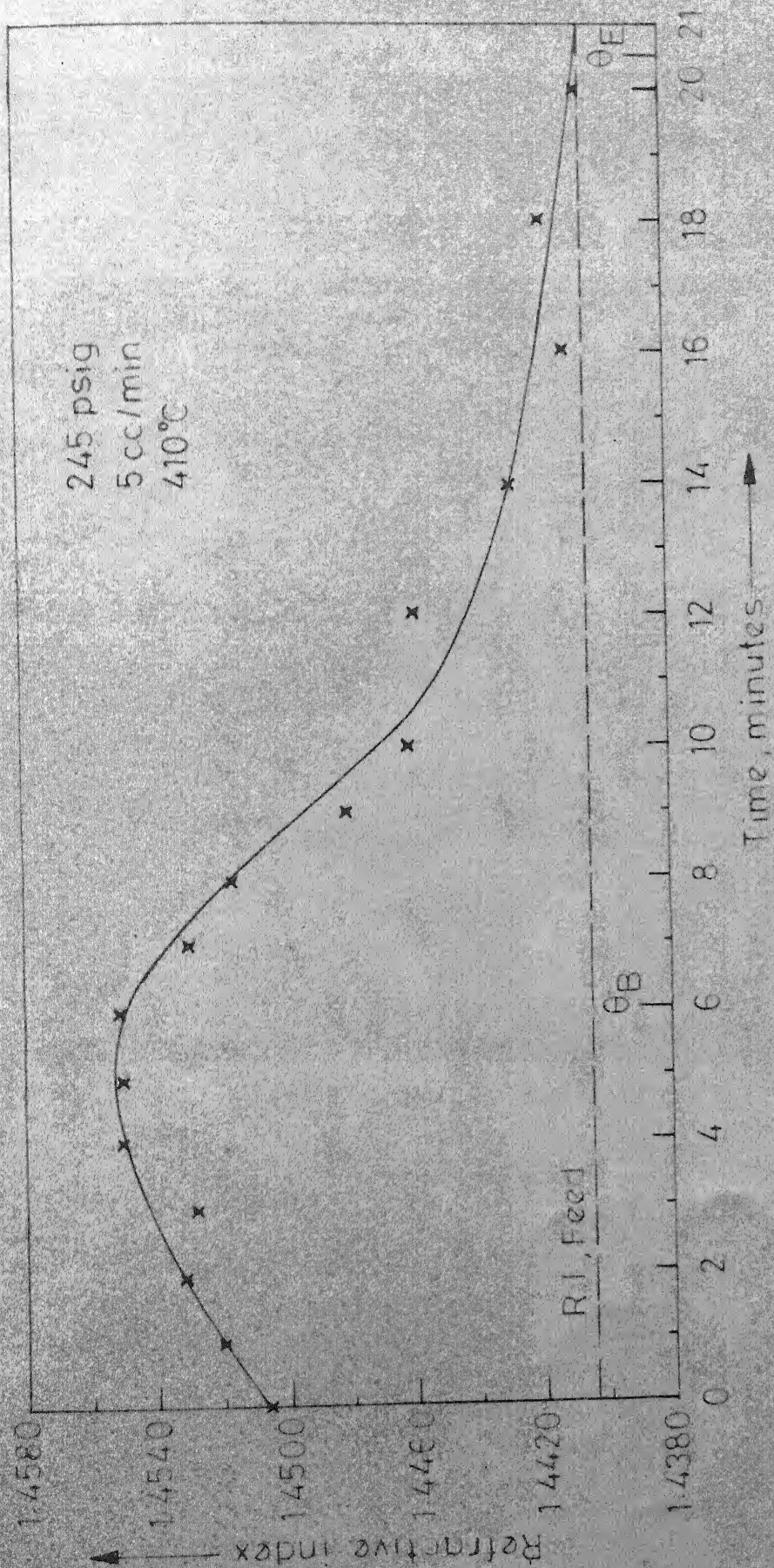


Fig. 8 - Breakthrough curve for Kerosene.

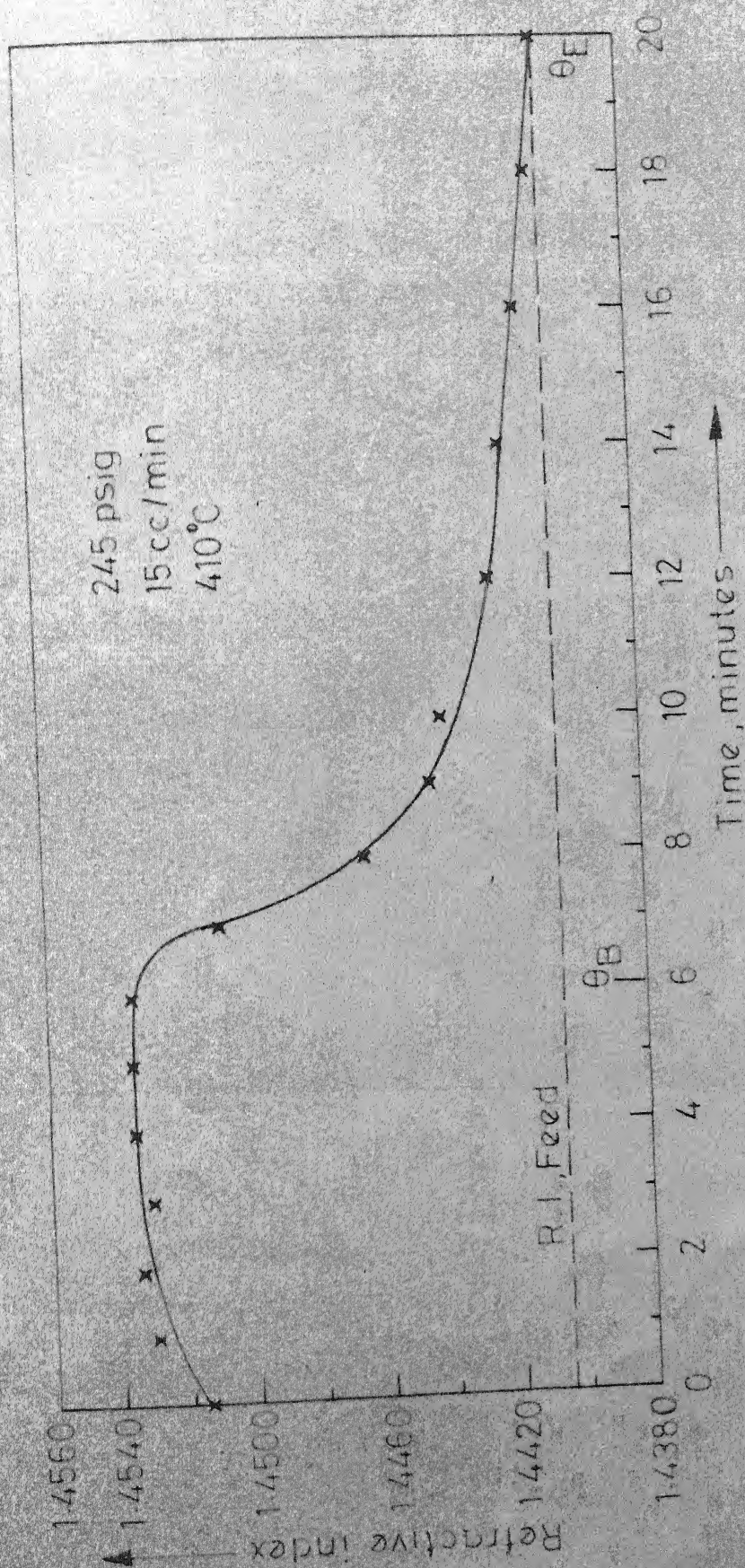


Fig 9 - Breakthrough curve for Kerosene

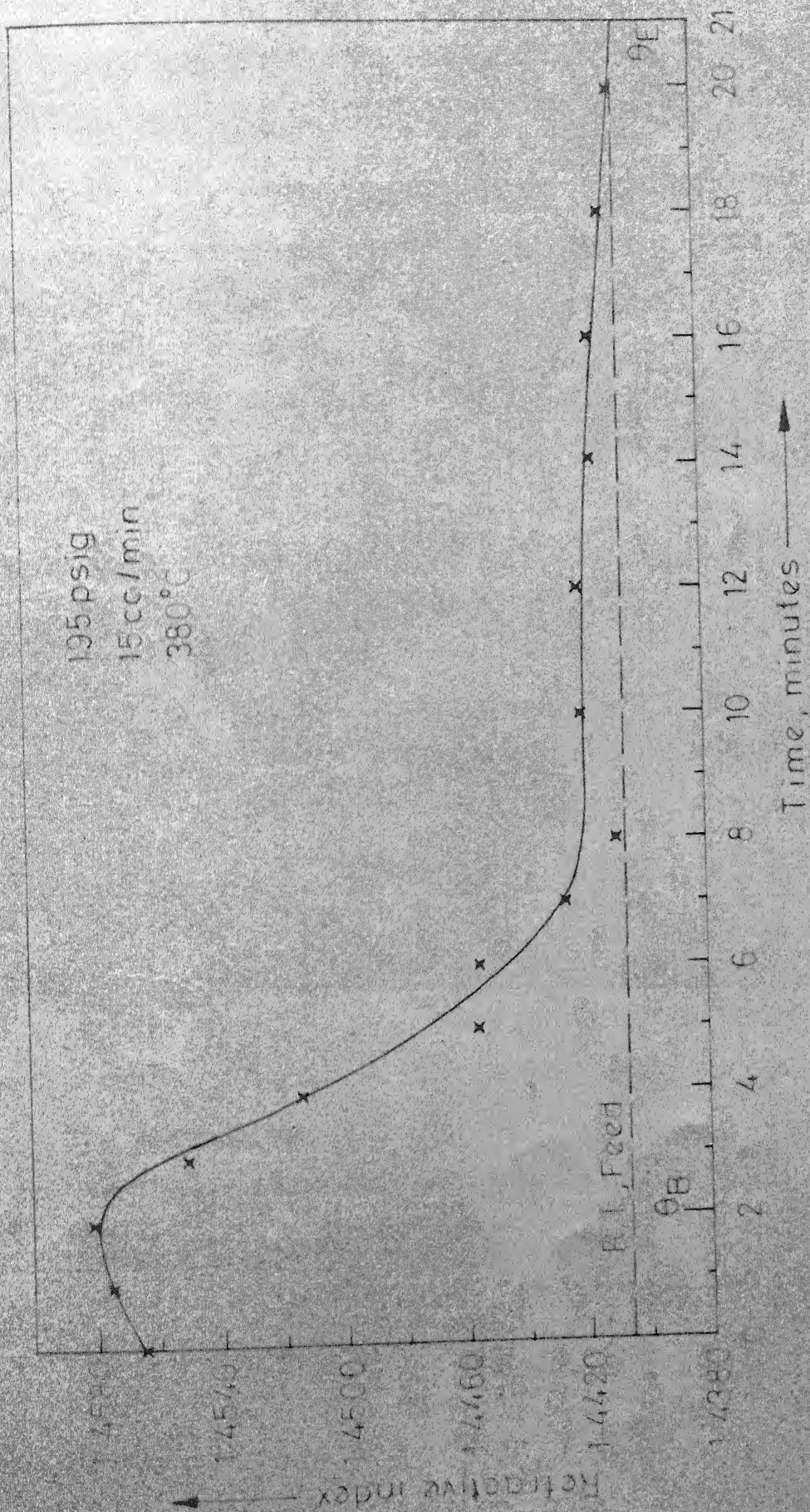


Fig. 10 - Breakthrough curve for Kerosene

of mass transfer zone and over-all mass transfer coefficient were calculated using the equations (2) and (4). The approximations were made as discussed in Chapter 4.

A comparative study of effect of various desorbent (Ammonia, nitrogen and LPG) on rate of desorption was carried out conducting two more runs at the optimum conditions. The effects are shown in Table II. The purity of recovered n-paraffins was established with the help of FIA method and GLC analysis. Smoke point was used as an indicator of quality of denormalized kerosene. The results are shown in Table I.

B. Discussion of Breakthrough Curves:

The experimental breakthrough curves were smooth and S shaped. They differed from an idealized breakthrough curve only in two respects: (1) they were slightly asymmetrical because the change in the slope of the trailing edge was slower than that of the leading edge. These findings were similar to the findings of Schumacher and York⁽¹³⁾ who worked for the separation of n-hexane from different constituents of kerosene using LMS-5A. These phenomena can be attributed to molecules getting adsorbed in cavities near the outer surface of pellets in the earlier stages of adsorption. As the cavities are filled, molecules have to diffuse through a large number of intercrystalline pores to find suitable (empty) cavities. (2): the other difference was the occurrence of rapid increase in concentration in the first 2-3 minutes of

adsorption. This can be attributed to the smaller height of adsorption column than the height of mass transfer zone.

From Table I, it can be seen that varying the pressure and flow rate affect the break point and exhaust point. However, the changes observed in the latter two quantities are not independent of each other. Their interaction has been obvious from values of θ_B and θ_E . Out of these two parameters, pressure effect seems to be the dominant parameter; and for optimization purposes, must be studied closely. Pressure and flow rates have got a reverse effect on the equilibrium loading. In general, as the pressure is increased, equilibrium loading also increases but at the optimum conditions, the effect is reverse. The effect of pressure is more in the pressure range of 175 to 250 psig. When the flow rate was changed from 10 to 40 cc/min at a pressure of 75/psig., the equilibrium loading changed by 5 cc., while the same amount of change in flow rate at 220 psig caused a change of 10 cc in equilibrium loading.

C. Results of Analysis:

The purity of n-paraffins recovered ranged from 90.3 to 95.6%. The main impurities were aromatics and naphthenes. With the help of FIA method percentage of aromatics was calculated. Assuming that aromatics and naphthenes adsorbed on intercrystalline surface, naphthene percentage present in the saturates was estimated to be half of the aromatics. This was done on the basis that aromatics and naphthenes will be adsorbed in the same

TABLE I

EXPERIMENTAL RESULTS FOR ADSORPTION CYCLE

| Run No. | Pressure psig | Temperature °C | Flow Rate cc/min. | Eqlbm. loading cc | Exhaust point min. | Break point min. | Purity of n-paraffins (PIA)% | Smoke point mm. | Value of objective function cc/min.Kg. |
|---------|---------------|----------------|-------------------|-------------------|--------------------|------------------|------------------------------|-----------------|--|
| 1. | 75 | 340 | 40 | 33 | 17 | 3 | 94.7 | 22.0 | 3.08 |
| 2. | 220 | 400 | 40 | 40 | 18 | 4 | 92.3 | 20.5 | 3.52 |
| 3. | 75 | 340 | 10 | 38 | 18.5 | 3 | 90.7 | 20.5 | 2.75 |
| 4. | 220 | 400 | 10 | 50 | 20 | 4 | 92.5 | 20.0 | 3.98 |
| 5. | 147 | 375 | 25 | 46 | 19 | 4 | 93.3 | 21.5 | 3.85 |
| 6. | 195 | 380 | 5 | 31.6 | 18.7 | 3 | 95.6 | 18.0 | 2.70 |
| 7. | 245 | 410 | 5 | 32 | 20.5 | 6 | 90.3 | 17.5 | 2.48 |
| 8. | 245 | 410 | 15 | 44 | 20 | 6 | 93.5 | 18.5 | 3.5 |
| 9. | 195 | 380 | 15 | 54 | 21 | 2 | 94.0 | 21.0 | 4.10 |

TABLE II

EXPERIMENTAL RESULTS FOR DESORPTION CYCLE

| Desorbant | Adsorptive Conditions | | | Pressure of Desorbent psig | Time for 90% Recovery (min) | Time for Total Recovery (min) |
|-------------|-----------------------|---------------------|-------------------|-------------------------------------|--------------------------------------|-------------------------------------|
| | Pressure psig | Flow Rate cc/min | Temperature °C | | | |
| Nitrogen | 195 | 15 | 380 | 5 | 30 | 60 |
| LPG(Indane) | 195 | 15 | 380 | 5 | 20 | 40 |
| Ammonia | 195 | 15 | 380 | 5 | 3 | 10 |

TABLE IIIHEIGHT OF MASS TRANSFER ZONE AND OVER-ALLMASS TRANSFER COEFFICIENT

| Run No. | Pressure psig. | Flow Rate cc/min. | H _z (Meter) | K _{ya} Kg/hour, Cu. m. |
|------------|-------------------|----------------------|---------------------------|------------------------------------|
| 1. | 75 | 40 | 1.64 | 3220 |
| 2. | 220 | 40 | 1.40 | 3780 |
| 3. | 75 | 10 | 1.56 | 845 |
| 4. | 220 | 10 | 1.71 | 770 |
| 5. | 147 | 25 | 1.16 | 2840 |
| 6. | 195 | 5 | 1.49 | 442 |
| 7. | 245 | 5 | 0.94 | 700 |
| 8. | 245 | 15 | 1.16 | 1700 |
| 9. | 195 | 15 | 2.30 | 860 |

TABLE IV
ANALYSIS OF RECOVERED n-PARAFFINS BY
GAS-LIQUID CHROMATOGRAPHY

Column substrate: 100% S.E. 30
 Column support: Celite 545
 Column temperature: 220°C
 Detector Temperature: 250°C
 Injector Temperature: 250°C
 Column length: 2 meters
 Carrier Gas: Hydrogen
 Flow Rate (Carrier Gas): 10 ml/min.
 Type of Detector: Thermal conductivity Detector
 Sample Volume: 6 l

| Carbon No. Run No. | C ₉ -C ₁₁ | C ₁₂ | C ₁₃ | C ₁₄ | C ₁₅ | C ₁₆ | C ₁₇ | Others |
|------------------------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------|
| 9 | 11.8 | 10.2 | 16.8 | 21.2 | 18.0 | 11.5 | 6.8 | 3.8 |
| 4 | 21.2 | 14.7 | 18.5 | 17.6 | 13.9 | 7.8 | 4.4 | 1.9 |
| Straight Run Kerosene (1) | 31.0 | 14.9 | 14.5 | 15.0 | 13.7 | 8.0 | 2.3 | 0.6 |

proportion as they are present in the bulk fluid.

The results of chromatographic analysis have been tabulated in Table 4. The carbon number distribution in recovered n-paraffins is shown along with that of n-paraffins in straight run kerosene. A typical chromatogram and a calibration table are attached in Appendix. Impurities, detected by FIA method, which constitutes 5 to 10% of the total recovery, were also verified by the chromatographic analysis. The resolution of first three peaks was not very sharp, so the compositions of C_9-C_{11} constituents have been lumped together, as shown in the Table 4. It is clear from Table 4, that the column is selective in adsorption for heavier components.

An important observation was made at the pressure of 245 psig (Boiling Point $-410^{\circ}C$). Olefin content in the recovered n-paraffins increased significantly and the smoke point of the denormalized kerosene went much below the specified standard by ISI. This suggests that cracking of hydrocarbons starts under these conditions. Thus the column should not be operated under these conditions of severity.

A plot of recovery has been made with pressure and flow rate as abscissa and ordinate respectively. A contour of constant recovery was drawn with dark line for interpolated region and with dotted line for extrapolated region. A dark horizontal line passing through 245 psig gives the maximum limit for pressure to get separation without cracking. The smoke points have also been shown in parenthesis on the same curve. The left region of line

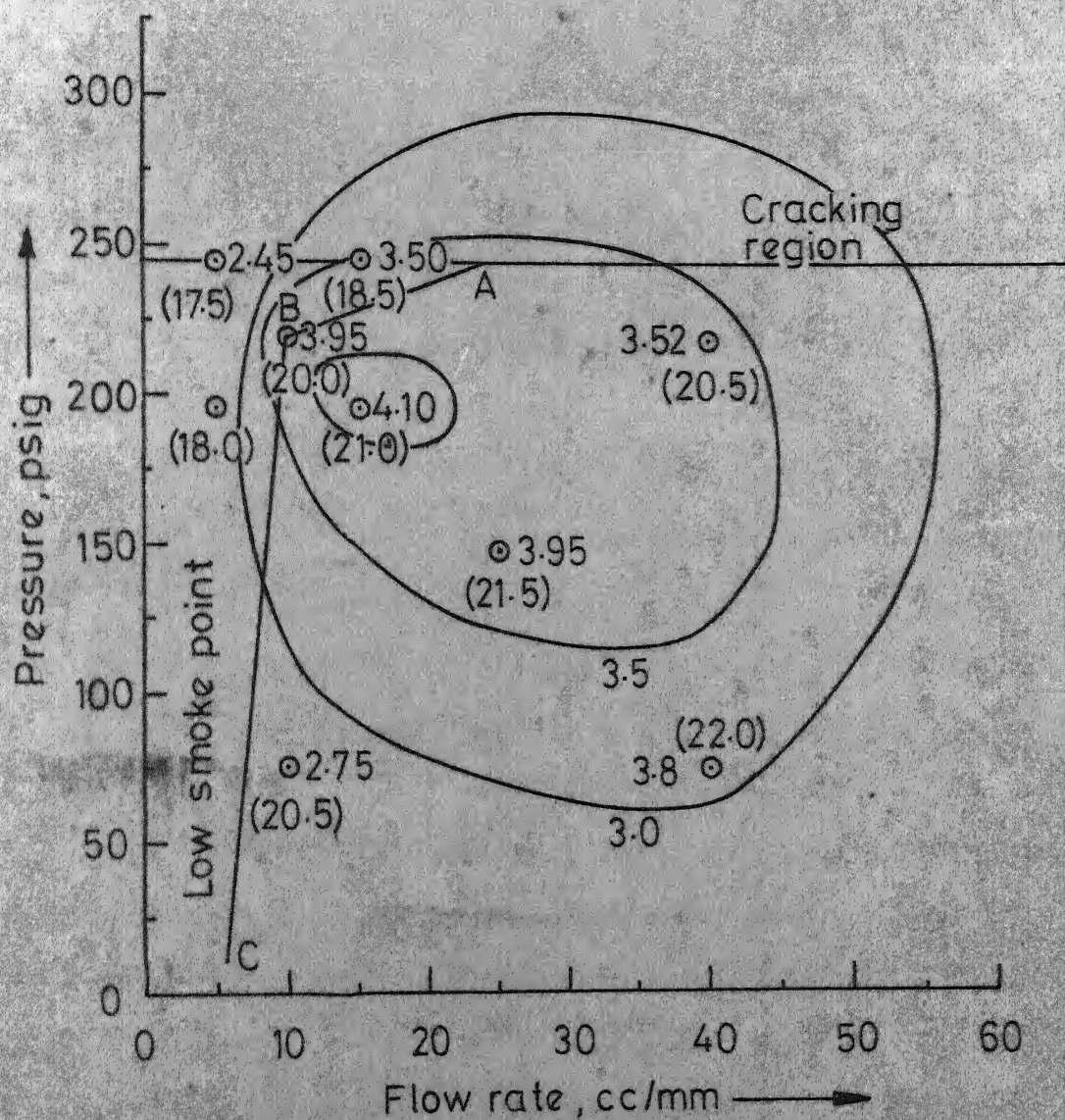


Fig. 11 - Plot of recovery and smoke point at experimental condition.

ABC gives smoke point less than the minimum standard of ISI. Thus one has to limit the optimum conditions below these limits of pressures and flow rates. The contours of constant smoke point could not be drawn for the present study.

The quality of denormalized kerosene was established by measuring its smoke point. The smoke point ranges from 17.5 to 22 mm. The lowering in smoke point can be attributed to a decrease in percentage of the remaining n-paraffins caused by the separation process or under certain conditions of severity by increasing the amount of olefins as a result of cracking. At the optimum conditions of separation, the percentage recovery was 19.6 and this corresponds to a yield of 39.2% of the total n-paraffins initially present in the straight run kerosene. The smoke point under the optimum conditions of recovery was 21 mm. The denormalized kerosene obtained under these conditions can be marketed as kerosene (since it satisfies ISI specifications). If, however, other operating conditions are selected, where the smoke point of the denormalized stock is low, it will have to be blended with the original kerosene to meet the minimum specifications of ISI.

D. Height of Mass Transfer Zone (H_z) and Over-all Mass Transfer Coefficient (K_{ya}):

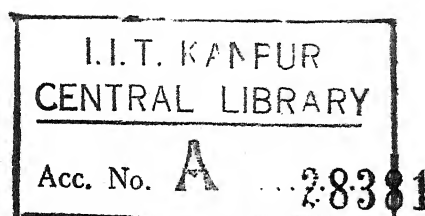
The validity of the MTZ model for the present system could not be established using the equation (3) in Chapter 4, as the detailed analysis of denormalized kerosenes was not possible. The height of mass transfer zone (H_z) and over-all mass transfer

coefficient (K_{ya}) were calculated (as discussed in Chapter 4) for each run and are tabulated in Table III. The over-all mass transfer coefficient was calculated with the approximation of over-all transfer unit ($N_t = 2.94$).

From Table III, one can see that pressure and flow rate have got reverse effect on the height of mass transfer zone. Increased flow rate increases the height of mass transfer zone while increased pressure reduces the height of mass transfer zone. These findings agree with the findings of workers^(13,36) for the system of n-hexane in benzene. Increased flow rate and pressure increases the over-all mass transfer coefficient. Flow rate seems to be more effective for over-all mass transfer coefficient. These findings are coherent to the findings of Schumacher and York⁽¹³⁾ but Kehat and Rosenkranz⁽³⁶⁾ has given the reverse effect of flow rate on over-all mass transfer coefficient. Generally, increased flow rate decreases the diffusional boundary layer decreasing the resistance to mass transfer. This may be one of the explanations for increase in over-all mass transfer coefficient.

E. Results of Desorption Cycle:

From Table II, it is clear that nitrogen as a desorbing gas was quite inefficient and took excessively long time. Performance of LPG was superior to that of nitrogen, cutting down the desorption time from 60 minutes to 40 minutes. These



results agree with those of Mahto, et al⁽²⁾ who used Naharkatiya crude fractions. Ammonia which was used for most of other runs, took the least time (10 minutes) for desorption. These results can be attributed to desorption mechanism involved with three gases. When nitrogen is used as desorbent, the driving force for desorption comes from the difference between the equilibrium vapor pressure of the adsorbate fluid and the actual partial pressure of the constituents of adsorbates in the purging stream (nitrogen).

In case of LPG, in addition to the purging action of adsorbed heavier paraffins, propane and butane present in it get adsorbed on the molecular sieves (displacing the already adsorbed heavier hydrocarbons).

Ammonia, because of its polar bonds, gets adsorbed on the molecular sieves even more strongly and hence it takes much less time for desorbing n-paraffins. Heat of adsorption of ammonia over LMS-5A is of the order of 10-12 Kcal/gmole which compensates the heat requirements for desorption of n-paraffins. Hence desorption cycle, with ammonia, can be operated at iso-thermal and isobaric conditions.

F. Implication of the Data for Design of an Adsorption Column:

The complete discussion of design data necessary to design full scale fixed adsorber is given in the appendix. The best operating conditions for an industrial operation will be

determined by an economic balance. This requires further study of remaining parameters given in the Appendix. However, considering that the design parameters studied in present work are the controlling parameters, this technically optimum will provide sufficient guideline to select the process conditions for given separation. The calculated height of mass transfer zone, equilibrium loading, over-all mass transfer coefficient and desorption rate study will provide data to specify the height, diameter and number of adsorption columns to be used for the desired separation.

* * *

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The optimum recovery of n-paraffins from Ankleshwar kerosene (140°-300°C) had been studied using the adsorption column of LMS-5A. Pressure and flow rate parameters had been optimized. The experiments were conducted using the modified two level factorial design and the direction of search were obtained with the help of EVOP method. The significant results are listed below:

- (1) The optimum recovery of 4.10 cc/min.Kg of adsorbent at the conditions of 195 psig (at 380°C) and 15 cc/min were obtained. The purity of recovered n-paraffins was above 94%.
- (2) The equilibrium loading at the optimum conditions was 54 cc for 0.63 Kg of adsorbent and increased with pressure.
- (3) The height of mass transfer zone and over-all mass transfer coefficient at the optimum conditions were 2.3 meters and 860 Kg/hr.cu.m. respectively.
- (4) The height of mass transfer zone decreased with pressure and increased with flow rate while over-all mass transfer coefficient increased with pressure and flow rate.

Recommendations:

- (1) The experiments can be carried out with the samples of naphtha and HSD to see the effect of feed concentration on optimum recovery.
- (2) More quantitative design data can be obtained using a longer coil (2-3 meters) for the adsorption column.
- (3) There is a need for a suitable liquid phase for GLC column, capable of better resolution of various components present in kerosene. Such analytical aid will be of great value for establishing the validity of MTZ model for the present system.

* * *

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APPENDIX

DESIGN OF A ADSORPTION COLUMN OF MOLECULAR SIEVES

Sufficient data must be obtained so that a commercial reactor may be designed with only a small number of design questions unanswered. Some of these unanswered questions may be like adsorbent life, best adsorbent particle size and optimum tube size, but still a reactor can be designed.

In the final design of a adsorption column, one has to consider the following items:

- (1) Pressure drop
- (2) Size and shape of solids
- (3) Heat transfer
- (4) Distribution of residence time (D_p/D_t) ratio)
- (5) Equilibrium data study
- (6) Kinetic data study
- (7) Specific surface, porosity and pore size (structure of solids)
- (8) Solid density and strength
- (9) Service life of solids

(1) Pressure Drop: It is necessary that pressure drop-flow rate relationship be measured under actual operating conditions in the development of apparatus. The results can be compared to the existing correlations

$$\frac{\Delta P}{L} = f(G, \epsilon, G, D_p, G)$$

a. The influence of total pressure is to be studied.

- a. It is possible to conceive of a "best" ΔP which would minimize the operating changes for the bed. Optimum is to be found between the following problems:
1. Larger particles give lower ΔP , reduce pumping cost but they are not efficient for reaction or mass transfer and heat transfer.
 2. Smaller particles give better efficiency, lower resistances to mass and heat transfer, better solid gas contact but they will give large ΔP .
- c. If gas is to be flow upwards, the gas flow rate must be below the fluidization velocity.
- d. The ΔP should not exceed 15% of total inlet pressure.

(2) Size and Shape of Solids: For regularly shaped pieces such as spheres or cylinder, there is a large amount of information on pressure drop, which could possibly be used for design purposes. For heat transfer physical properties of the solids do not matter appreciably. Shape and size affect effectiveness of adsorption also in addition to ΔP . It is considered wise to keep the ratio of tube size and solid particle size as 20:1, for reasons of gas distribution and wall effects.

(3) Heat Transfer: The overall coefficient contain three terms - (1) convective heat transfer coefficient on outside of solids retaining wall, (2) convective coefficient between process fluid and inside of solids retaining wall. (3) effective thermal conductivity of the bed of solids containing the moving

process fluid. The determination of the heat released during adsorption is important to the engineer since the heat released can reduce the effectiveness of the adsorbent. Plot of ^{log} pressure versus $1/T$ can give heat of adsorption by the formula

$$\frac{d \ln P}{d\left(\frac{1}{T}\right)} = - \frac{\Delta H}{R}$$

where P = partial pressure, psia

T = absolute temperature, °R.

(4) Particle Size-Tube Size Ratio: One has to see the effect of axial and radial diffusion inside the reactor.

(5) Equilibrium and Kinetic Study: Various workers have tried various kinetic models, linear, Langmuir, Volmer and B.E.T. isotherms assuming certain mechanism for mass transfer. The predicted results by these models could not agree with experimental results. Michaels has proposed the Mass Transfer Zone model. The model is based on the existence of an transfer zone of constant length across which the fluid concentration changes from 0.05 to 0.95 of initial concentration. Definition of mass transfer zone, its assumptions, validity and limitations of the model have been discussed in Chapter 4.

Calculation of MTZ Height:

The height of mass transfer zone can be calculated considering the definition and assumptions as given in Chapter 3. The time, θ_z , required for the transfer zone to move its own

height down through the bed under steady-state conditions is proportional to the volume of effluent, V_z (see Fig. A-2).

$$\theta_z = \frac{V_z}{U_L A} \quad (1)$$

where U_L = liquor flow rate (cm/sec), based on total column cross-section and A = total column cross-sectional area (sq.cm) similarly, the time, θ_T , required for the zone to establish itself at the top of the bed and to move down out of the bed is proportional to the total volume of effluent collected, V_T :

$$\theta_E = V_E / (U_L A) \quad (2)$$

Except for the period of time during which it is being formed at the beginning of the process, θ_F , the zone is descending through the bed at a constant rate determined by

$$U_z = \frac{H_T}{\theta_E - \theta_F} \quad (3)$$

The height of the mass transfer zone must be determined by the relation

$$H_z = U_z \theta_z = H_T \left(\frac{\theta_z}{\theta_E - \theta_F} \right) \quad (4)$$

The only unknown in equation (4) is θ_F . However, this time can be estimated quite closely in the following manner:

The quantity of asorbate removed by the transfer zone from the breakthrough point to exhaustion of the bed may be determined graphically from

$$Q_z = \int_{V_B}^{V_E} (X_0 - X) dV \quad (5)$$

where Q_z = total adsorbate removed by transfer zone, V_B = volume of effluent collected upto breakthrough point, X_0 = concentration of adsorbed component in influent and X = concentration of component in effluent. If, however, the mass transfer rate has been infinite, the removal would have been equal to (nearly)

$$Q_{z \max} = X_0 V_z \quad (6)$$

Hence the fraction of the exchanger present in the zone which still possesses the ability to remove components is

$$F = \frac{Q_z}{Q_{z \max}} = \frac{V_E}{V_B} \frac{\int (X_0 - X) dV}{X_0 V_z} \quad (7)$$

If $F=0$, it would be expected that the time formation of the zone at the top of the bed would be nearly equal to the time required for the zone to descend a distance equal to its own height, θ_z , after S.S. is reached. Conversely, if $F=1$, the time of formation of the zone would be very short. A simple relation for estimating zone formation time which satisfies the limiting conditions is as follows:

$$\theta_F = (1-F) \theta_z \quad (8)$$

On a basis of these assumptions one can calculate the height of the exchange zone from the breakthrough curve and the relation

$$H_z = H_T \left(\frac{Q_z}{Q_E - (1-F) \theta_z} \right) = H_T \left(\frac{V_z}{V_E - (1-F) V_z} \right) \quad (9)$$

The height of MTZ, based on solute material balance can be given as

$$H_z = \frac{Q_z}{A (C_s - X_{sF})} \quad (10)$$

where the notations are the same as used in Chapter 4. The bed capacity for adsorption can be calculated as

$$C_B = \frac{\int_0^{V_B} (C_o - C) dV}{V_R} \quad (11)$$

$$C_E = \frac{\int_0^{V_E} (C_o - C) dV}{V_R} \quad (12)$$

where C_E = total capacity of bed; C_B = effective capacity of the bed. The overall mass transfer coefficient can be calculated as

$$H_z = \frac{G_s}{K_{ya}} \int_{y_B}^{y_E} \frac{dy}{y - y^*} = \frac{G_s N_t}{K_{ya}} \quad (13)$$

where the notations are the same as given in Chapter 4.

Parameters Affecting the Height of MTZ (H_z) and K_{ya} .

- (1) Temperature
- (2) Pressure
- (3) Flow rate
- (4) Size and shape of particles
- (5) Feed concentration
- (6) Length and diameter of bed
- (7) Adsorbent
- (8) Previous history of the bed.

Desorption Cycle Study:

As discussed in Chapters (2) and (3), the desorption cycle is a crucial step for designing a complete column. Any of swings - thermal, pressure, purging, displacement or combination, can be used for the cycle. There can be following parameters to be studied for obtaining the desorption time.

- (1) initial loading
- (2) desorption pressure
- (3) operating temperature
- (4) length of linear hydrocarbons

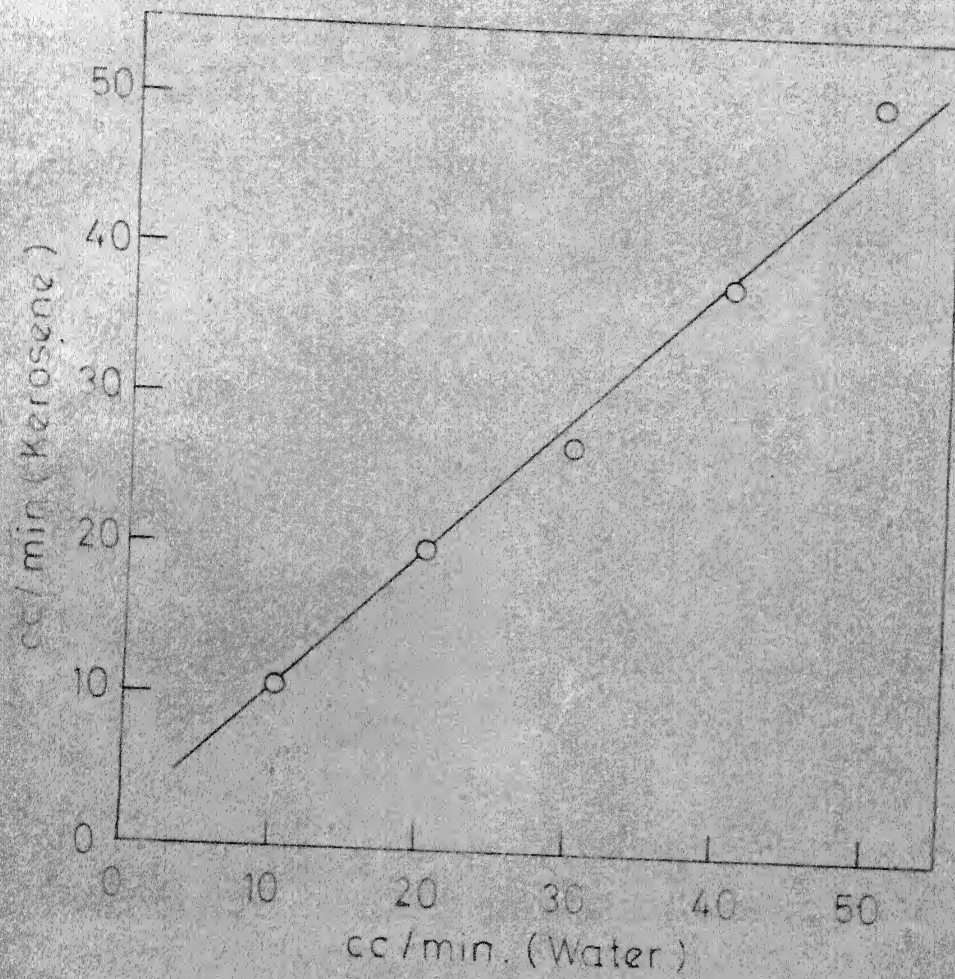
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Fig.A1 - Calibration of rotameter.

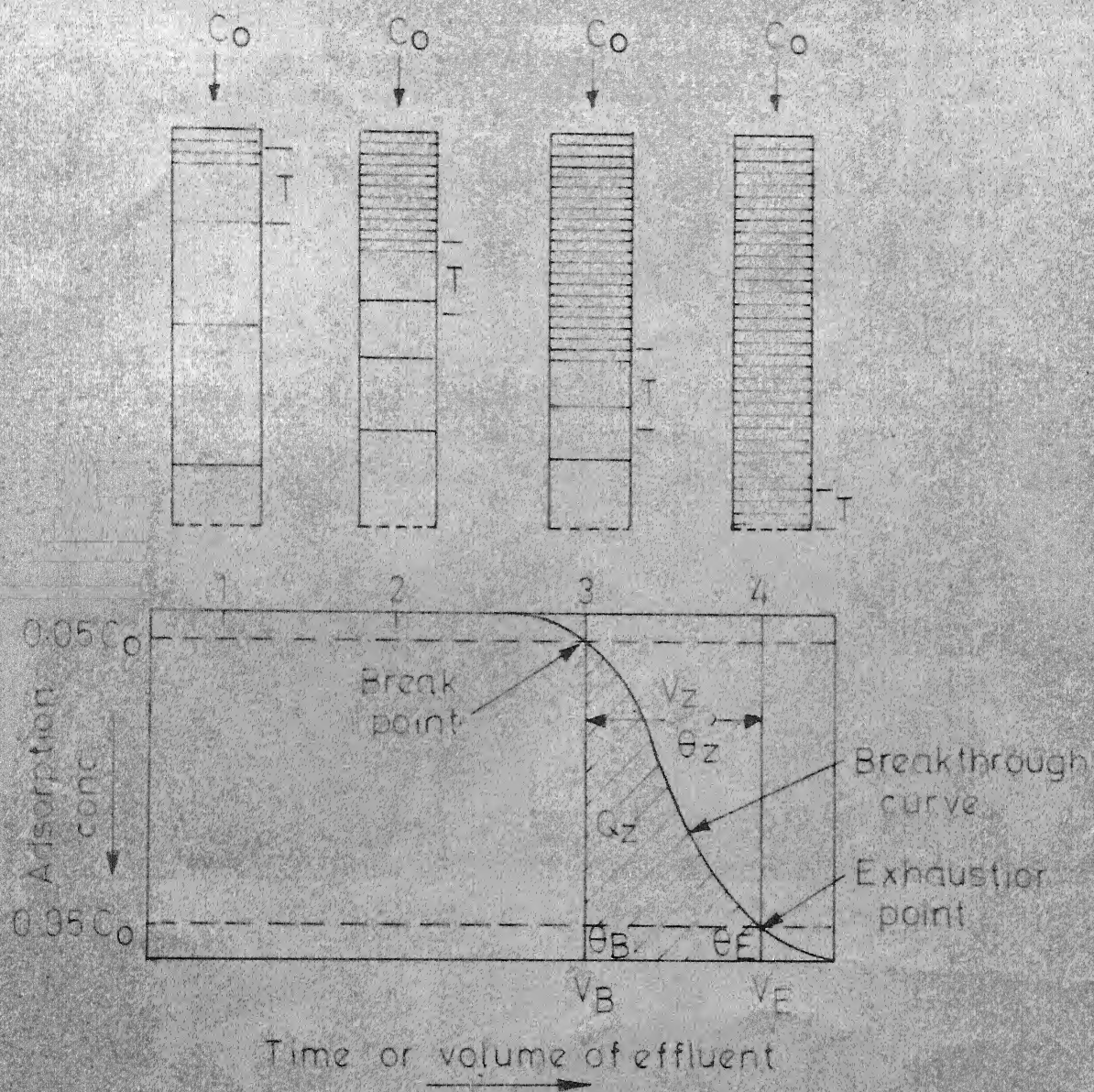


Fig A2 - Adsorption column behavior

TABLE A-1CALIBRATION OF CHROMATOGRAMS USING PURE SAMPLES

Chart Speed: 12"/hr.

| Carbon Number | Retention Time(min.) | Height of Peak (mm.) |
|------------------|-------------------------|-------------------------|
| C ₉ | 2.9 | 120 |
| C ₁₀ | 3.3 | 100 |
| C ₁₃ | 5.5 | 85 |
| C ₁₆ | 11.5 | 28 |
| C ₁₇ | 15.5 | 13 |

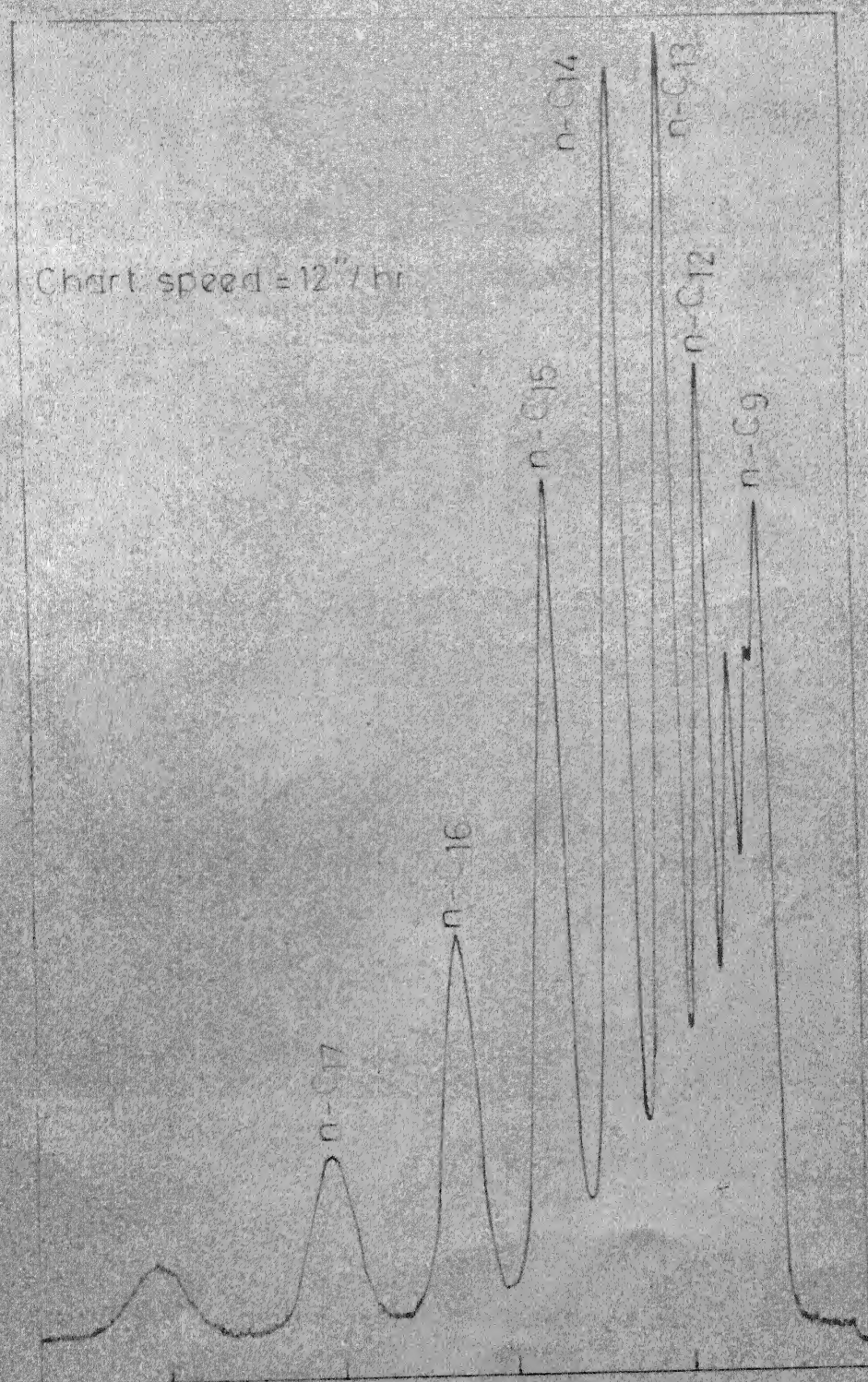


Fig A3 - Chromatograms of n-Paraffins from Run no. 3

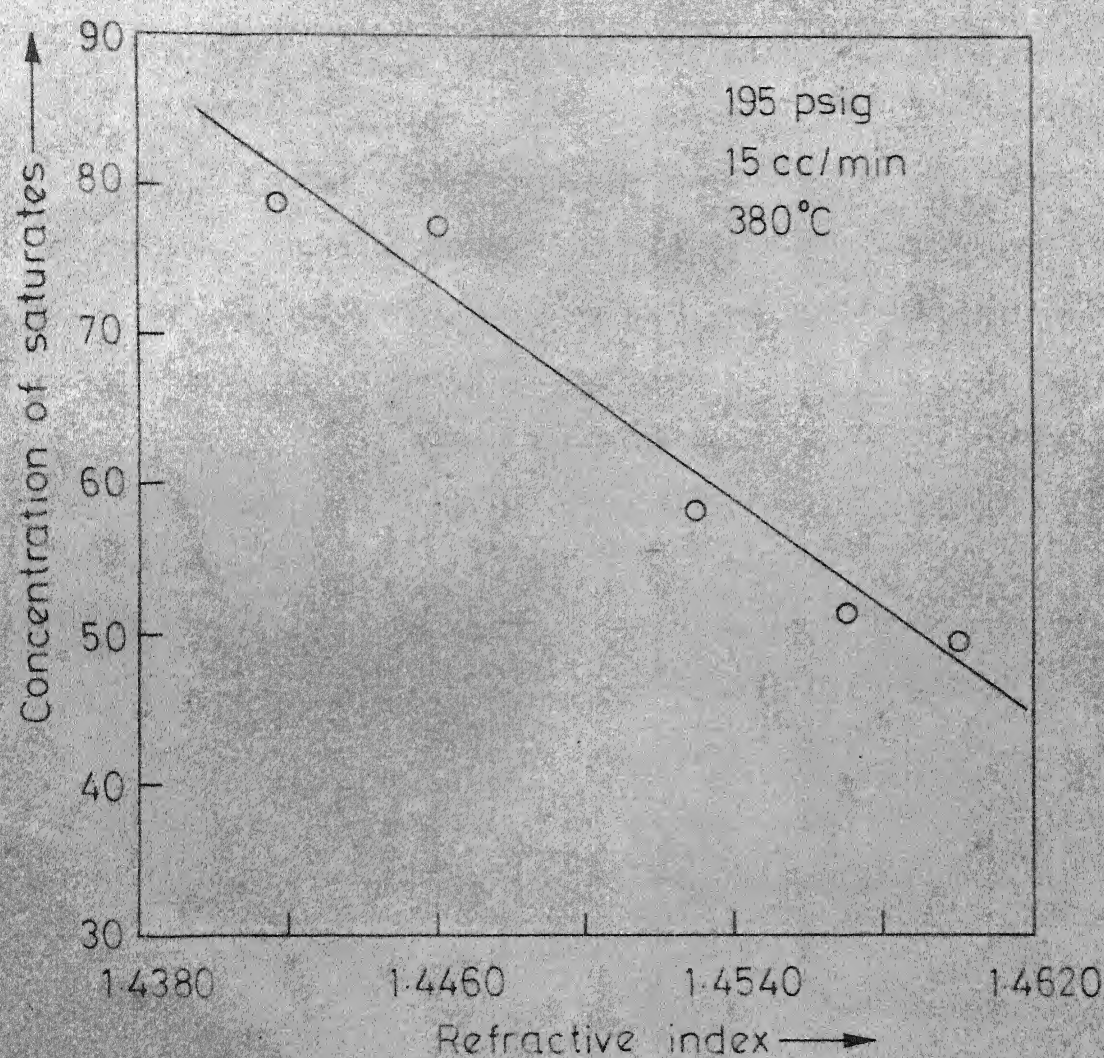


Fig A4 - Plot of concentration of saturates and refractive index of denormalized kerosene.

POST-SCRIPT

These explanations have been added to clarify the results and analysis as desired by the examiners of the thesis.

1. The linear relationship was obtained by plotting concentration of saturates (measured by FIA method) versus refractive index of denormalized samples. The plot is shown in Fig.A-4.

2. The denormalized kerosene, used for smoke point measurement, included some amount of kerosene collected after the exhaustion point. This amount was not more than 10% of total denormalized stock in any case.

3. The maximum value of H_2 and low value of K_{ya} at the optimum condition in Table III, may be because of following reasons.

a. The linearity of relationship between refractive index and concentration of saturates was not checked for other cases. Values of H_2 and K_{ya} strongly depend on nature of breakthrough curves. If the relation is not linear, the curve may change slightly. In such a case, the absolute values of these quantities may change significantly.

4. The adsorption column used for the experimental study consisted of copper pipe (82 cm x 3.7 I.D.) packed with 630 gms of molecular sieves (1/16" pellets) upto the height of 74 cms. The bed porosity was 0.43 and D_t/D_p ratio was 24.